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These notes are concenred with the generalization of 3D growth theory based on mixture theory.

General Theory of Surface Growth based on Mixture Theory

1 Introduction

2 Preliminaries. Mixture of two species.

We are concerned with a body that grows by the addition or removal of new material at its boundary. Imagine a body comprised of a polymer network that is surrounded and infused by a solvent of monomers. The monomers, carried by the solvent, can enter or exit from the body at its boundaries, and they can diffuse through the body. In addition, when thermodynamically favorable, a monomer molecule may attach (by "association") or detach (by "dissociation") from a polymer chain, which we assume to happen on the boundary of the body. Therefore at a point on the boundary, a monomer molecule can either (a) attach to a polymer chain and so become part of the body, (b) detach from a polymer chain and so be expelled from the body, (c) infiltrate between the polymer chains and diffuse into the body, or (d) a previously infiltrated monomer molecule can diffuse out of the body.

In order to keep track of the different (species undergoing these different) processes we find it helpful to formulate the problem using the framework of mixture theory[1]. Our intention is not to use mixture theory per se to solve the problem, only to develop and motivate a suitable theory. In keeping track of each individual species, as well as the transformation between species, it will sometimes be helpful to speak of "particles" (or even "molecules") even though we will always be working within a continuum theory.

Since association and dissociation are assumed to only occur on the boundary, the continuum theory in the interior of the body is effectively a fairly standard one describing a fluid infiltrated solid or a hydrogel, e.g. [8, 7, 13, 17]. It is the conditions at the boundary that are nonstandard. However it is not convenient to use mixture theory on the boundary and some other theory in the interior and so we develop the entire theory within the single framework of mixture theory.

Consider a mixture of two species, species-1 and -2. When specialized to the context described above, we take species-1 to be an elastic solid corresponding to the polymeric body and species-

[1] Our description of mixture theory is limited in many ways, e.g. it neglects inertial and thermodynamic effects. For a complete description of mixture theory the reader may refer to, e.g. Bowen [5] and Truesdell and Toupin [27].

2 to be an inviscid fluid corresponding to the monomeric fluid. Keep in mind that in the class of problems of interest, species-2 can transform into species-1 by association and species-2 can transform into species-1 by dissociation.

Each species undergoes a motion

$$\mathbf{y} = \boldsymbol{\chi}_\alpha(\mathbf{x}_\alpha, t), \qquad \alpha = 1, 2, \tag{2.1}$$

where $\mathbf{x}_\alpha$ denotes the position of a particle of species-α in a reference configuration *for that species.* Mixture theory is based on the key modeling assumption that two particles $\mathbf{x}_1$ and $\mathbf{x}_2$, one from each species, can occupy the same position $\mathbf{y}$ in the current configuration, Truesdell [26]; see also Fick [10] and Stefan [23]. The index α is understood to take the values 1 and 2. No summation over α is implied, even if this index is repeated.

Let $\mathcal{R}_t$ denote the region of physical space occupied by the body at time t and let $\mathcal{R}_{R\alpha}(t)$ be the corresponding region in the reference space for species-α. Thus $\mathbf{y} \in \mathcal{R}_t$ and $\mathbf{x}_\alpha \in \mathcal{R}_{R\alpha}(t)$. While there is an underlying reference space associated with each species, we will rarely need to consider that of species-2 – the fluid. Therefore *whenever we refer to "the reference space" we mean the reference space for species-1. Likewise when we say, for example, mass or energy per unit reference volume, we mean per unit volume in the reference space of species-1.* The region $\mathcal{R}_{R1}(t)$ is often referred to as the region occupied by the "dry solid".

Note that the region $\mathcal{R}_t$ in physical space changes due to both the diffusion of species-2 through it ("swelling") and growth. On the other hand the referential region $\mathcal{R}_{R1}(t)$ is time dependent only due to growth when particles are being added to and removed from the solid body.

Looking ahead, once we have completed developing the theory of interest, the only species we will need to explicitly consider in reference space will be species-1, and so at that point we will drop the subscript 1 from, for example, $\mathbf{x}_1$ and $\mathcal{R}_{R1}(t)$.

At each instant t the mapping (2.1) from $\mathcal{R}_{R\alpha}(t) \to \mathcal{R}_t$ is required to be invertible. Let $\mathbf{x}_\alpha = \widehat{\mathbf{x}}_\alpha(\mathbf{y}, t)$ denote its inverse. An arbitrary smooth field ζ can be written in the alternative equivalent forms $\zeta(\mathbf{y}, t)$ and $\widehat{\zeta}(\mathbf{x}_\alpha, t)$ where $\widehat{\zeta}(\mathbf{x}_\alpha, t) = \zeta(\boldsymbol{\chi}_\alpha(\mathbf{x}_\alpha, t), t)$ and $\zeta(\mathbf{y}, t) = \widehat{\zeta}(\mathbf{x}_\alpha(\mathbf{y}, t), t)$. Moreover, observe that any field $\widehat{g}(\mathbf{x}_2, t)$ associated with species-2 can be expressed in the form $\overline{g}(\mathbf{x}_1, t)$ by mapping $\mathcal{R}_{R2}(t) \to \mathcal{R}_t \to \mathcal{R}_{R1}(t)$ whence

$$\overline{g}(\mathbf{x}_1, t) = \widehat{g}(\widehat{\mathbf{x}}_2(\boldsymbol{\chi}_1(\mathbf{x}_1, t), t), t).$$

For simplicity we shall omit symbols such as the hat $\widehat{(\cdot)}$ except when it maybe confusing not to do so.

When expressed in terms of $\mathbf{y}$ and t we denote the partial derivatives of a field ζ by

$$\frac{\partial \zeta}{\partial t} = \frac{\partial \zeta}{\partial t}(\mathbf{y}, t), \qquad \text{grad}\, \zeta = \frac{\partial \zeta}{\partial \mathbf{y}}(\mathbf{y}, t), \tag{2.2}$$

and when expressed in terms of $\mathbf{x}_\alpha$ and t we write

$$\frac{D_\alpha \zeta}{Dt} = \frac{\partial \zeta}{\partial t}(\mathbf{x}_\alpha, t), \qquad \text{Grad}_\alpha \zeta = \frac{\partial \zeta}{\partial \mathbf{x}_\alpha}(\mathbf{x}_\alpha, t). \tag{2.3}$$

Thus in particular, $D_\alpha(\cdot)/Dt$ is the time rate of change at a fixed species-α particle $\mathbf{x}_\alpha$. The operations $\partial/\partial t$, div and grad on ζ take for granted that the field has been expressed spatially as a function of $\mathbf{y}$ and t and so we will omit the argument of $\zeta(\mathbf{y}, t)$.

The particle velocities, deformation gradient tensors and Jacobian determinants associated with the motions $\mathbf{y} = \boldsymbol{\chi}_\alpha(\mathbf{x}_\alpha, t)$ are

$$\mathbf{v}_\alpha = \frac{\partial \boldsymbol{\chi}_\alpha}{\partial t}(\mathbf{x}_\alpha, t), \qquad \mathbf{F}_\alpha = \frac{\partial \boldsymbol{\chi}_\alpha}{\partial \mathbf{x}_\alpha}(\mathbf{x}_\alpha, t) \qquad \text{and} \qquad J_\alpha = \det \mathbf{F}_\alpha, \tag{2.4}$$

respectively, and the corresponding velocity gradient tensors are

$$\mathbf{L}_\alpha = \operatorname{grad} \mathbf{v}_\alpha = \frac{\partial \mathbf{v}_\alpha}{\partial \mathbf{y}}(\mathbf{y}, t). \tag{2.5}$$

Let ρ_α denote the mass density of species-α in the current configuration, i.e. the mass of species-α in a unit volume of the mixture in the current configuration. Then the mass density ρ of the mixture and its velocity $\mathbf{v}$ are defined by

$$\rho \;\coloneqq\; \rho_1 + \rho_2, \qquad \rho\mathbf{v} \;\coloneqq\; \rho_1\mathbf{v}_1 + \rho_2\mathbf{v}_2. \tag{2.6}$$

The mass of species-α per unit volume in the reference space of species-α is

$$\rho_{R1} = \rho_1 J_1, \qquad \rho_{R2} = \rho_2 J_2. \tag{2.7}$$

It is useful to introduce

$$c_R \;\coloneqq\; \rho_2 J_1, \tag{2.8}$$

which denotes the *mass of species-2 per unit reference volume (of species-1)*.

Next, consider the motion of species-2 through (relative to) species-1. This will be characterized by the mass flux vector $\mathbf{j}$ representing the mass of species-2 (per unit area per unit time) crossing a surface in the current configuration that is material[2] with respect to species-1:

$$\mathbf{j} \;\coloneqq\; \rho_2(\mathbf{v}_2 - \mathbf{v}_1). \tag{2.9}$$

Roughly speaking, whenever we encounter the quantity $\rho_2\mathbf{v}_2$ in our calculations below, we shall use (2.9) to replace it with $\mathbf{j}$.

Finally let the free energy per unit mass and the ("partial") Cauchy stress tensor associated with species-α be ψ_α and $\mathbf{T}_\alpha$ respectively. Then the free energy per unit mass of the mixture, ψ, and the mixture stress, $\mathbf{T}$, are defined by

$$\rho\psi \;\coloneqq\; \rho_1\psi_1 + \rho_2\psi_2, \qquad \mathbf{T} \;\coloneqq\; \mathbf{T}_1 + \mathbf{T}_2, \tag{2.10}$$

respectively. We do not include inertial effects in our analysis. Had we retained such effects, this would influence the notions of the mixture free energy and stress, e.g. see section 1.4 of Bowen [5].

[2] A surface is material with respect to species-1 if it is attached to the same species-1 particles at all times.

2.1 Basic equations for each species.

In the interior of the body there is no transformation between the species, i.e. monomer molecules are not converted into polymer molecules or vice versa, and so the number of particles of each species is individually conserved. Consider an arbitrary region $D_1(t)$ in the interior of the body that is *material with respect to species*-1, i.e. it follows the same set of species-1 particles at all times. Then the respective *mass balance* statements for species-1 and species-2 require

$$\frac{d}{dt}\int_{D_1} \rho_1\, dV_y = 0, \qquad \frac{d}{dt}\int_{D_1} \rho_2\, dV_y + \int_{\partial D_1} \rho_2(\mathbf{v}_2 - \mathbf{v}_1)\cdot \mathbf{n}\, dA_y = 0. \tag{2.11}$$

The second term in the second equation characterizes the mass influx of species-2 across the boundary ∂D_1 that moves at the velocity $\mathbf{v}_1$. When localized, the first of these gives the mass balance field equation for species-1,

$$\rho_{R1} = \rho_1 J_1; \tag{2.12}$$

see (2.7). Similarly $(2.11)_2$ yields the mass balance field equation for species-2,

$$\frac{\partial \rho_2}{\partial t} + \text{div}\,(\mathbf{j} + \rho_2\mathbf{v}_1) = 0, \tag{2.13}$$

where the mass flux vector $\mathbf{j}$ was introduced in (2.9). We have written the two preceding local mass balance statements in different forms since we have in mind that species-1 is a solid and species-2 a fluid. Equation (2.13) can be written as

$$\frac{1}{J_1}\frac{D_1 c_R}{Dt} + \text{div}\,\mathbf{j} = 0, \tag{2.14}$$

where D_1/Dt and c_R were introduced in (2.3) and (2.8) respectively.

The referential mass flux of species-2 through species-1, defined by

$$\mathbf{j}_R \;:= = J_1\mathbf{F}_1^{-1}\mathbf{j}, \tag{2.15}$$

is readily shown to obey

$$\mathbf{j}\cdot\mathbf{n}\, dA_y = \mathbf{j}_R\cdot\mathbf{n}_R\, dA_x, \tag{2.16}$$

where $\mathbf{n}$ and dA_y are a unit normal vector and differential element of area on a surface in the current configuration and $\mathbf{n}_R$ and dA_x are the corresponding quantities on its image in the reference configuration. The mass balance equation (2.14) can alternatively be written as

$$\frac{D_1 c_R}{Dt} + \text{Div}_1\,\mathbf{j}_R(\mathbf{x}_1, t) = 0, \tag{2.17}$$

where $\text{Div}_1\,\mathbf{j}_R = \mathbf{F}_1\cdot\text{grad}\,\mathbf{j}_R$.

Force balance for each species in the absence of externally applied body forces requires

$$\int_{D_1} \mathbf{T}_1\mathbf{n}\, dA_y + \int_{D_1} \rho_1\mathbf{p}_1\, dV_y = 0, \qquad \int_{D_1} \mathbf{T}_2\mathbf{n}\, dA_y + \int_{D_1} \rho_2\mathbf{p}_2\, dV_y = 0. \tag{2.18}$$

The term $\rho_1 \mathbf{p}_1$ is the force per unit current volume applied on species-1 by species-2 due to the relative motion between the two species, the so-called "diffusive drag force". Likewise the term $\rho_2 \mathbf{p}_2$ is the corresponding force applied by species-2 on species-1. We assume these forces to be equal in magnitude and opposite in direction and denote the common value by $\mathbf{p}$:

$$\mathbf{p} := \rho_2 \mathbf{p}_2 = -\rho_1 \mathbf{p}_1. \tag{2.19}$$

Localizing (2.18) and keeping (2.19) in mind yields the force balance field equations

$$\text{div } \mathbf{T}_1 - \mathbf{p} = \mathbf{0}, \qquad \text{div } \mathbf{T}_2 + \mathbf{p} = \mathbf{0}. \tag{2.20}$$

For simplicity we shall assume that one species does not apply a couple on the other species. Then, one can show that *moment balance* requires

$$\mathbf{T}_1 = \mathbf{T}_1^T, \qquad \mathbf{T}_2 = \mathbf{T}_2^T.$$

Internal couples between the species can be accounted for, e.g., see section 1.4 of Bowen [5].

2.2 Basic equations for the mixture.

Mass balance in the interior of the body requires

$$\frac{d}{dt} \int_{D_1} \rho_1 \, dV + \frac{d}{dt} \int_{D_1} \rho_2 \, dV + \int_{\partial D_1} \rho_2 (\mathbf{v}_2 - \mathbf{v}_1) \cdot \mathbf{n} \, dA = 0, \tag{2.21}$$

where again $D_1(t)$ is an arbitrary region that is material with respect to species-1. The third term characterizes the mass influx across the boundary ∂D_1 that moves at the velocity $\mathbf{v}_1$. The associated field equation is readily shown to be

$$\frac{\partial \rho}{\partial t} + \text{div } (\mathbf{j} + \rho \mathbf{v}_1) = 0, \tag{2.22}$$

where the mixture mass density ρ and the flux $\mathbf{j}$ were defined in $(2.6)_1$ and (2.9) respectively. Since $\rho \mathbf{v} = \rho_1 \mathbf{v}_1 + \rho_2 \mathbf{v}_2 = \rho \mathbf{v}_1 + \mathbf{j}$ this can be written in the familar form

$$\frac{\partial \rho}{\partial t} + \text{div } (\rho \mathbf{v}) = 0. \tag{2.23}$$

Force balance in the absence of external body forces requires

$$\int_{D_1} (\mathbf{T}_1 \mathbf{n} + \mathbf{T}_2 \mathbf{n}) \, dA_y = 0, \tag{2.24}$$

with associated field equation

$$\text{div } \mathbf{T} = \mathbf{0}, \tag{2.25}$$

where the mixture stress $\mathbf{T}$ was defined in $(2.10)_2$. Observe that the diffusive drag force $\mathbf{p}$ does not appear in (2.24) and (2.25), reflecting the fact that, from the perspective of the mixture, this is an internal force. Similarly moment balance for the mixture requires

$$\mathbf{T} = \mathbf{T}^T. \tag{2.26}$$

Finally we turn to the **dissipation inequality** for the mixture. It is not necessary that we write separate dissipation inequalities for each species (though we can do so). Associated with each species we allow for the possibility that, in addition to the free energy per unit mass ψ_α, there may be an energy source e_α (representing the amount of species-α energy created per unit mass per unit time) due to interaction with the other species. Moreover, we account for the work done by the diffusive drag force which we take to be $\rho_\alpha \mathbf{p}_\alpha \cdot \mathbf{v}_\alpha$. However, we assume that the totality of the internal interaction terms do not contribute to the energetics of the mixture in the sense that

$$\sum_{\alpha=1}^{2} \left(\rho_\alpha e_\alpha + \rho_\alpha \mathbf{p}_\alpha \cdot \mathbf{v}_\alpha\right) = 0. \tag{2.27}$$

Accordingly, for each region D_1 that is material with respect to species-1 we postulate that the rate of increase of free energy cannot exceed the power of the forces acting on it plus the influx of free energy:

$$\begin{aligned} \int_{\partial D_1} (\mathbf{T}_1\mathbf{n}\cdot\mathbf{v}_1 + \mathbf{T}_2\mathbf{n}\cdot\mathbf{v}_2)\, dA_y \; + \int_{\partial D_1} -\rho_2\psi_2(\mathbf{v}_2 - \mathbf{v}_1)\cdot\mathbf{n}\, dA_y \;\geq \\ \geq \; \frac{d}{dt}\int_{D_1} \rho\psi \, dV_y. \end{aligned} \tag{2.28}$$

This can be written equivalently using (2.9) and $(2.10)_2$ as

$$\int_{\partial D_1} \mathbf{T}\mathbf{n}\cdot\mathbf{v}_1 \, dA_y \; + \int_{\partial D_1} (\mathbf{T}_2 - \rho_2\psi_2\mathbf{I})(\mathbf{v}_2 - \mathbf{v}_1)\cdot\mathbf{n}\, dA_y \;\geq\; \frac{d}{dt}\int_{D_1}\rho\psi\, dV_y. \tag{2.29}$$

The local form of this is readily shown to be

$$\mathbf{T}\cdot \operatorname{grad}\mathbf{v}_1 + \mathbf{T}_2\cdot\operatorname{grad}(\mathbf{v}_2 - \mathbf{v}_1) - \operatorname{div}(\psi_2\mathbf{j}) + \psi\operatorname{div}\mathbf{j} - \mathbf{p}\cdot(\mathbf{v}_2 - \mathbf{v}_1) \geq \rho\frac{D_1\psi}{Dt} \tag{2.30}$$

where the time derivative D_1/Dt was defined in (2.3).

2.3 A kinematic constraint.

Before turning to the constitutive equations we first describe a kinematic constraint – "intrinsic incompressibility" – that we assume to hold. Here, each species is taken to be individually incompressible though this does not imply that the mixture is incompressible (since the amount of each species in a unit volume of the mixture need not stay constant).

Consider a region of the mixture of volume ΔV_y in physical space whose image in the reference space for species-α has volume $\Delta V_{x\alpha}$. Then

$$\Delta V_y = J_\alpha \Delta V_{x\alpha} \qquad \text{where } J_\alpha = \det \mathbf{F}_\alpha.$$

Let $\Delta V_{y\alpha}$ be the volume of the part of ΔV_y occupied by species-α, so that in particular

$$\Delta V_y = \Delta V_{y1} + \Delta V_{y2}.$$

When we say that each species is individually incompressible we mean that

$$\Delta V_{y1} = \Delta V_{x1}, \qquad \Delta V_{y2} = \Delta V_{x2}.$$

It follows from the three preceding equations that

$$\frac{1}{J_1} + \frac{1}{J_2} = 1. \tag{2.31}$$

This can be written in terms of the mass densities by using (2.7):

$$\frac{\rho_1}{\rho_{R1}} + \frac{\rho_2}{\rho_{R2}} = 1. \tag{2.32}$$

Finally we write this in terms of the quantity c_R introduced in (2.8). Recall that c_R represents the mass of species-2 per unit reference volume of species-1, i.e. $c_R = \rho_2 \Delta V_y / \Delta V_{x1} = \rho_2 J_1$. We can now write

$$J_1 \overset{(2.31)}{=} 1 + \frac{J_1}{J_2} \overset{(2.7)}{=} 1 + \frac{J_1}{\rho_{R2}/\rho_2} \overset{(2.8)}{=} 1 + \frac{c_R}{\rho_{R2}}.$$

On setting

$$\nu \;:=\; 1/\rho_{R2}, \tag{2.33}$$

we can express the preceding equation as

$$J_1 = 1 + \nu c_R. \tag{2.34}$$

We take ν to be a constant.

It will be useful for future purposes to note from the preceding equations that

$$\rho_1 = \frac{\rho_{R1}}{1 + \nu c_R}, \qquad \rho_2 = \frac{c_R}{1 + \nu c_R}, \qquad \rho = \frac{\rho_{R1} + c_R}{1 + \nu c_R}, \tag{2.35}$$

and that the mass of mixture per unit reference volume is

$$\rho_R := \rho J_1 = \rho_1 J_1 + \rho_2 J_1 = \rho_{R1} + c_R. \tag{2.36}$$

As a final observation, note by differentiating (2.34) with respect to time at fixed $\mathbf{x}_1$ and using the identity $D_1 J_1 / Dt = J_1 \operatorname{div} \mathbf{v}_1$ that

$$J_1 \operatorname{div} \mathbf{v}_1 = \nu \frac{D_1 c_R}{Dt}. \tag{2.37}$$

This, together with the mass balance equation (2.14), leads to the field equation

$$\operatorname{div}(\mathbf{v}_1 + \nu \mathbf{j}) = 0. \tag{2.38}$$

Remark for Rami Tal paper: Let ϕ be the volume of species-2 per unit mixture volume in the current configuration, i.e.

$$\phi = \frac{\Delta V_{y2}}{\Delta V_y} = \frac{\Delta V_{x2}}{\Delta V_y} = \frac{1}{J_2} = \frac{\rho_2}{\rho_{R2}} = \nu\rho_2 = \frac{\nu c_R}{1+\nu c_R} = \frac{\phi_R}{1+\phi_R}, \tag{2.39}$$

where

$$\phi_R = \frac{\Delta V_{y2}}{\Delta V_{x1}} = \phi J_1 = \nu c_R = J_1 - 1,$$

is the species-2 (solvent) volume in the mixture per unit volume in the reference configuration. Then

$$\rho_1 = (1-\phi)\rho_{R1}, \qquad \rho_2 = \phi\rho_{R2},$$

and

$$\phi = \frac{J_1 - 1}{J_1}, \qquad J_1 = \frac{1}{1-\phi}.$$

Also define the volumetric flux by

$$\mathfrak{h} = \nu\mathbf{j} = \nu\rho_2(\mathbf{v}_2 - \mathbf{v}_1) = \phi(\mathbf{v}_2 - \mathbf{v}_1).$$

and chemical potential

$$\tilde{\mu} = \mu/\nu.$$

2.4 Constitutive equations.

We now turn to the constitutive relations and assume species-1 to be an elastic solid and species-2 to be an inviscid fluid. Accordingly we take the constitutive response functions for stress and free energy to be functions of $\mathbf{F}_1$ and ρ_2: $\mathbf{T}_\alpha = \mathbf{T}_\alpha(\mathbf{F}_1, \rho_2), \psi_\alpha = \psi_\alpha(\mathbf{F}_1, \rho_2)$. Since $\rho_1 = \rho_{1\mathrm{R}}/\det \mathbf{F}_1$ it is not necessary to include ρ_1 as an argument in the response functions. It turns out to be more convenient to express the primitive constitutive response functions in the equivalent form

$$\mathbf{T} = \mathbf{T}(\mathbf{F}_1, c_R), \qquad \mathbf{T}_2 = \mathbf{T}_2(\mathbf{F}_1, c_R), \qquad \varphi = \varphi(\mathbf{F}_1, c_R), \qquad \psi_2 = \psi_2(\mathbf{F}_1, c_R), \tag{2.40}$$

where

$$\varphi := J_1\, \rho\psi \tag{2.41}$$

is the Helmholtz free energy (of the mixture) *per unit reference volume*, and $c_R = \rho_2 J_1$, introduced previously in $(2.8)_1$, represents the mass of species-2 per unit reference volume. As for the diffusive drag force $\mathbf{p}$, it is natural to assume that in addition to $\mathbf{F}_1$ and ρ_2, it also depends on the relative velocity[3] $\mathbf{v}_2 - \mathbf{v}_1$ between the two species. Therefore we assume the diffusive drag force law to have the form

$$\mathbf{p} = \widehat{\mathbf{p}}(\mathbf{F}_1, \rho_2, \mathbf{j}) \tag{2.42}$$

[3]Though each velocity $\mathbf{v}_1$ and $\mathbf{v}_2$ is not material frame indifferent, their difference $\mathbf{v}_2 - \mathbf{v}_1$ is.

where $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$.

Using (2.40) and (2.42) in the local dissipation inequality (2.30) and simplifying using the Coleman-Noll argument in the presence of the kinematic constraint (2.38), leads to the following constitutive relations

$$\mathbf{T} = \frac{1}{J_1}\frac{\partial \varphi}{\partial \mathbf{F}_1}\mathbf{F}_1^T - q\,\mathbf{I}, \qquad \mathbf{T}_2 = -\rho_2\,(\mu - \psi_2)\,\mathbf{I}, \tag{2.43}$$

where we have set

$$\mu = \frac{\partial \varphi}{\partial c_R} + \nu q. \tag{2.44}$$

The field q here arises as a result of the kinematic constraint. Observe that the constitutive relation $(2.43)_1$ for $\mathbf{T}$ only involves the free energy φ of the mixture while $(2.43)_2$ involves both φ and ψ_2. The reduced dissipation inequality now reads

$$\Big(\widehat{\mathbf{p}}(\mathbf{F}_1, \rho_2, \mathbf{j}) + \rho_2 \mathrm{grad}\,\mu - \mathrm{grad}\,\rho_2(\mu - \psi_2)\Big)\cdot \mathbf{j} \le 0. \tag{2.45}$$

This can be further reduced using the equilibrium equation $\mathrm{div}\,\mathbf{T}_2 + \mathbf{p} = \mathbf{0}$, the constitutive equation $\mathbf{T}_2 = -\rho_2\,(\mu - \psi_2)\,\mathbf{I}$ and $\mathbf{p} = \widehat{\mathbf{p}}(\mathbf{F}_1, \rho_2, \mathbf{j})$ to

$$\mathrm{grad}\,\mu \cdot \mathbf{j} \le 0. \tag{2.46}$$

The dissipation inequality (2.29) can now be rewritten in light of the constitutive relation $(2.43)_2$ in the illuminating form

$$\int_{\partial D_1} \mathbf{Tn}\cdot \mathbf{v}_1\, dA_y \;\ge\; \frac{d}{dt}\int_{D_1} \rho\psi\, dV_y + \int_{\partial D_1} \mu\,\mathbf{j}\cdot\mathbf{n}\, dA_y, \tag{2.47}$$

from which we identify the scalar μ as being the *chemical potential*[4] per unit mass of species-2. Note that μ was not introduced as a primitive quantity when formulating the theory above. Rather, it arose out of the individual free energies of the species. In the particular case where ψ_1 is independent of ρ_2, one can readily show that

$$\mu = \frac{\partial}{\partial \rho_2}(\rho_2\psi_2) + \nu q,$$

so that the chemical potential μ is directly related to the fluid free energy ψ_2.

Finally note that the equation of motion of species-2, $\mathrm{div}\,\mathbf{T}_2 + \mathbf{p} = \mathbf{0}$ simplifies because of $(2.43)_2$ to

$$\mathbf{p} = \mathrm{grad}\,\big[\rho_2(\mu - \psi_2)\big]. \tag{2.48}$$

Therefore if, for example, we take the diffusive drag force law to be

$$\widehat{\mathbf{p}}(\mathbf{F}_1, \rho_2, \mathbf{j}) = \mu\,\mathrm{grad}\,\rho_2 - \mathrm{grad}(\rho_2\psi_2) - m^{-1}\,\mathbf{j}, \tag{2.49}$$

where m is a constant, the species-2 equation of motion (2.48) reduces to

$$\mathbf{j} = -m\,\rho_2\,\mathrm{grad}\,\mu. \tag{2.50}$$

In this case the dissipation inequality (2.46) holds automatically provided $m > 0$.

[4]See Bowen [5] for a more general discussion of the chemical potential.

2.5 Summary.

Given the mixture free energy $\varphi(\mathbf{F}_1, c_R)$, the fluid free-energy $\psi_2(\mathbf{F}_1, c_R)$ and the diffusive drag force response function $\widehat{\mathbf{p}}(\mathbf{F}_1, c_R, \mathbf{j})$ the following system of equations is to be solved for the motion $\boldsymbol{\chi}_1$, the flux $\mathbf{j}$ and the fluid density c_R:

$$\text{Force balance for mixture} \qquad \mathbf{div}\,\mathbf{T} = \mathbf{0}. \tag{2.51}$$

$$\text{Force balance for species} - 2 \qquad \mathbf{p} = \text{grad}\big[\rho_2(\mu - \psi_2)\big]. \tag{2.52}$$

$$\text{Mass balance for species} - 1 \qquad \rho_{R1} = \rho_1 J_1. \tag{2.53}$$

$$\text{Mass balance for species} - 2 \qquad \frac{1}{J_1}\frac{D_1 c_R}{Dt} + \text{div}\,\mathbf{j} = 0. \tag{2.54}$$

$$\text{Kinematic constraint} \qquad J_1 = 1 + \nu c_R. \tag{2.55}$$

$$\text{Constitutive equation for mixture stress} \qquad \mathbf{T} = \frac{1}{J_1}\frac{\partial\varphi}{\partial\mathbf{F}_1}\mathbf{F}_1^T - q\,\mathbf{I}. \tag{2.56}$$

$$\text{Constitutive equation for chemical potential} \qquad \mu = \frac{\partial\varphi}{\partial c_R} + \nu q. \tag{2.57}$$

$$\text{Diffusive drag force law} \qquad \mathbf{p} = \widehat{\mathbf{p}}(\mathbf{F}_1, \rho_2, \mathbf{j}). \tag{2.58}$$

$$\text{Reduced dissipation inequality} \qquad \mathbf{j}\cdot\text{grad}\,\mu \le 0. \tag{2.59}$$

where $\mathbf{F}_1 = \text{Grad}_1\boldsymbol{\chi}_1$, $J_1 = \det\mathbf{F}_1$, $\rho_2 = c_R/J_1$ and $\nu = 1/\rho_{R2}$.

3 Conditions on the boundary derived from Mixture Theory.

3.1 Kinematics of boundary motion.

Before turning to the boundary conditions per se, it is first necessary to characterize the motion of the boundary, and in particular, to distinguish between the motion of a point of the surface of the body and the material point that happens to be at that same location at that instant.

Recall that in the current configuration the body occupies a region $\mathcal{R}_t$, and a species-1 material point is located at $\mathbf{y} = \boldsymbol{\chi}_1(\mathbf{x}_1, t) \in \mathcal{R}_t$. As mentioned previously, the only reference configuration we need to consider, unless explicitly stated otherwise, is that for species-1. In this (dry solid) configuration a species-1 material point is located at $\mathbf{x}_1 \in \mathcal{R}_{R1}(t)$.

Let $\mathbf{n}$ and $\mathbf{n}_R$ denote the respective unit outward normal vectors at corresponding points on the surfaces $\partial\mathcal{R}_t$ and $\partial\mathcal{R}_{R1}$ in the current and reference configurations, and let dA_y and dA_x be corresponding differential area elements. These are related by

$$\mathbf{n}\,dA_y = J_1\mathbf{F}_1{}^{-\mathrm{T}}\mathbf{n}_R\,dA_x; \tag{3.1}$$

e.g. see Chapter 2, eqn. (21) of Chadwick [6]. For any field g, we write g^+ and g^- for its limiting values at a point on $\partial\mathcal{R}_t$ when the point is approached from, respectively, the positive and negative side, the positive side being that into which $\mathbf{n}$ points. The positive side therefore corresponds to the outside of the body, the negative side to the inside. We write $[\![g]\!] = g^+ - g^-$ for the jump in g across $\partial\mathcal{R}_t$.

Since species-1 does not exist outside the body we will not encounter terms such as $\mathbf{v}_1^+, \mathbf{F}_1^+$ and ψ_1^+. Therefore any quantity at $\partial\mathcal{R}_t$ associated with species-1 must necessarily be on the inner side and the superscript must necessarily be a minus sign. Thus we can safely drop this superscript and adopt the convention that *whenever we write* $\mathbf{v}_1, \mathbf{F}_1, \psi_1$ *etc. at* $\partial\mathcal{R}_t$ *for species-1 it is understood that these represent* $\mathbf{v}_1^-, \mathbf{F}_1^-, \psi_1^-$ *etc.* While we will adopt this convention in what follows, occasionally, for clarity, we shall explicitly display the minus sign on quantities related to species-1. Note that we have already adopted this convention in equation (3.1) by not writing $\mathbf{F}_1^-$ and J_1^-. On the other hand species-2 exists both inside and outside the body and so we must always keep the $\pm$ labels on quantities pertaining to species-2 at $\partial\mathcal{R}_t$.

When growth occurs, the reference configuration is time dependent and therefore so is the region $\mathcal{R}_{R1}$. Consider a point $\mathbf{x}_b(t)$ on the boundary $\partial\mathcal{R}_{R1}$ in the reference configuration and let its image in the current configuration be $\mathbf{y}_b(t) = \boldsymbol{\chi}_1(\mathbf{x}_b(t), t) \in \partial\mathcal{R}_t$. The respective velocities $\mathbf{V}_R$ and $\mathbf{V}$ of these two *boundary points* are $\mathbf{V}_R = \dot{\mathbf{x}}_b(t)$ and $\mathbf{V} = \dot{\mathbf{y}}_b(t)$. Differentiating $\mathbf{y}_b(t) = \boldsymbol{\chi}_1(\mathbf{x}_b(t), t)$ with respective to time yields the following relation between the boundary velocities $\mathbf{V}, \mathbf{V}_R$, particle velocity $\mathbf{v}_1$ and deformation gradient tensor $\mathbf{F}_1$:

$$\mathbf{V} = \mathbf{F}_1\mathbf{V}_R + \mathbf{v}_1, \tag{3.2}$$

where $\mathbf{v}_1$ and $\mathbf{F}_1$ were defined in (2.4). Observe that in general the velocity $\mathbf{V}$ of a point of the boundary differs from the velocity $\mathbf{v}_1$ of the (species-1) material point that happens to be at that same location at that time[5]. If there is no growth, the referential region $\mathcal{R}_{R1}$ is time independent and so $\mathbf{V}_R = \mathbf{0}$ and thus $\mathbf{V} = \mathbf{v}_1$.

Let $V_R = \mathbf{V}_R \cdot \mathbf{n}_R$. Then if $V_R > 0$ at some point on $\partial\mathcal{R}_{R1}$, the referential boundary is moving outwards at that point and so material is being added to the body. This corresponds to association. Similarly $V_R < 0$ corresponds to dissociation. Thus

$$\text{Association} : V_R > 0, \qquad \text{Dissociation} : V_R < 0. \tag{3.5}$$

To describe this in terms of the motion of the boundary $\partial\mathcal{R}_t$ in the current configuration, we first

[5]Skalak et al. provide a careful discussion of the kinematics of surface growth in [21]. In particular they refer to the velocity with which "material points move away from the surface of growth",

$$\mathbf{V}_G = \mathbf{v}_1 - \mathbf{V}, \tag{3.3}$$

as the *growth velocity*. Note from (3.2) and (3.3) that

$$\mathbf{V}_G = -\mathbf{F}_1\mathbf{V}_R, \tag{3.4}$$

whence $\mathbf{V}_G = \mathbf{0}$ if and only if $\mathbf{V}_R = \mathbf{0}$. Skalak et al. [22] point out that the growth velocity $\mathbf{V}_G$ need not be perpendicular to the growth surface, and study the geometry of various structures that arise from different choices of the direction of $\mathbf{V}_G$.

observe from (3.1) and (3.2) that

$$(\mathbf{V} - \mathbf{v}_1) \cdot \mathbf{n}\, dA_y = J_1\, \mathbf{V}_R \cdot \mathbf{n}_R\, dA_x. \tag{3.6}$$

Thus association $V_R > 0$ corresponds to $(\mathbf{V} - \mathbf{v}_1) \cdot \mathbf{n} > 0$. In this case the point of the surface $\partial \mathcal{R}_t$ is instantaneously moving faster than the material point located at that same position. Therefore a volume $(\mathbf{V} - \mathbf{v}_1) \cdot \mathbf{n}\, dA_y$ "opens up" and is filled by new particles that are added to the body. Similarly dissociation $V_R < 0$ corresponds to $(\mathbf{V} - \mathbf{v}_1) \cdot \mathbf{n} < 0$ when the boundary is moving more slowly than the material point and so a volume $(\mathbf{v} - \mathbf{V}) \cdot \mathbf{n}\, dA_y$ is "lost" due to the detachment of particles.

The rate at which solid material (species-1) is being added to the body (mass per unit time)

$$= \rho_{R1}\, V_R\, dA_x = \rho_1\, (\mathbf{V} - \mathbf{v}_1) \cdot \mathbf{n}\, dA_y, \tag{3.7}$$

where we have used (3.6) and (2.12) in getting to the second expression. Here $V_R = \mathbf{V}_R \cdot \mathbf{n}_R$ is the normal velocity of the referential surface $\partial \mathcal{R}_{R1}$ and $\rho_{R1} = \rho_1 J_1$ is the referential mass density of species-1. At a point where dissociation is taking place this quantity will be negative and it would represent the rate at which solid is being lost from the body.

3.2 Mass balance.

The mass inflow (per unit area per unit time) of species-α *into* $\partial \mathcal{R}_t$ from inside the body is $\rho_\alpha^-(\mathbf{v}_\alpha^- - \mathbf{V}) \cdot \mathbf{n}$, and the mass outflow of species-α (per unit area per unit time) *away* from $\partial \mathcal{R}_t$ into the outside is $\rho_\alpha^+(\mathbf{v}_\alpha^+ - \mathbf{V}) \cdot \mathbf{n}$. These particles carry both mass and energy. Since a particle of one species can transform by association/dissociation into the other species, the mass of each individual species is not conserved, but the total mass is.

The mass (per unit area per unit time) of all particles flowing into $\partial \mathcal{R}_t$ from the inside is $\rho_1^-(\mathbf{v}_1^- - \mathbf{V}) \cdot \mathbf{n} + \rho_2^-(\mathbf{v}_2^- - \mathbf{V}) \cdot \mathbf{n}$, whereas the total outflow of particles away from $\partial \mathcal{R}_t$ into the outside is $\rho_2^+(\mathbf{v}_2^+ - \mathbf{V}) \cdot \mathbf{n}$. Balancing these mass flows yields

$$\rho_1^-(\mathbf{v}_1^- - \mathbf{V}) \cdot \mathbf{n} + \rho_2^-(\mathbf{v}_2^- - \mathbf{V}) \cdot \mathbf{n} = \rho_2^+(\mathbf{v}_2^+ - \mathbf{V}) \cdot \mathbf{n} \qquad \text{on } \partial \mathcal{R}_t. \tag{3.8}$$

The term $\rho_2 \mathbf{v}_2$ on the left-hand side can be eliminated in favor of the flux $\mathbf{j}$ to get

$$\rho^-(\mathbf{v}_1^- - \mathbf{V}) \cdot \mathbf{n} + \mathbf{j}^- \cdot \mathbf{n} = \rho_2^+(\mathbf{v}_2^+ - \mathbf{V}) \cdot \mathbf{n} \qquad \text{on } \partial \mathcal{R}_t, \tag{3.9}$$

though the same cannot be done on the right-hand side since $\mathbf{j}$ has no meaning outside the body. This is because our definition $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$ represents the flux of species-2 relative to species-1 and there are no species-1 particles on the outside.

It is natural therefore to write (3.8) in terms of a different notion of flux, one that is more intuitive at a moving surface. Accordingly let

$$\mathbf{h} := \rho_2(\mathbf{v}_2 - \mathbf{V}) \tag{3.10}$$

denote the flux of species-2 across a surface moving with velocity $\mathbf{V}$. The corresponding referential flux $\mathbf{h}_R$ obeys

$$\mathbf{h}\cdot\mathbf{n}\,dA_y = \mathbf{h}_R\cdot\mathbf{n}_R\,dA_x. \tag{3.11}$$

We can now write (3.8) as

$$[\![\mathbf{h}\cdot\mathbf{n}]\!] = \rho_1(\mathbf{v}_1 - \mathbf{V})\cdot\mathbf{n} \qquad \text{on } \partial\mathcal{R}_t, \tag{3.12}$$

(having dropped the minus sign from ρ_1 and $\mathbf{v}_1$ per our previously mentioned convention). This in turn can be written in referential form by using (3.7) and (3.11) as

$$\Big[\!\!\Big[\mathbf{h}_R\cdot\mathbf{n}_R\Big]\!\!\Big] = \rho_{R1}V_R \qquad \text{on } \partial\mathcal{R}_{R1}. \tag{3.13}$$

This says that the change in the flux $\mathbf{h}_R\cdot\mathbf{n}_R$ of species-2 across the boundary is balanced by the growth rate $\rho_{R1}V_R$.

Note that it is the flux $\mathbf{j}$, not $\mathbf{h}$, that appears in the field equations, e.g. (2.14) and (2.38).

3.3 Dissipation and driving force associated with growth.

We now consider the dissipation rate associated with growth. The net inflow of free energy into $\partial\mathcal{R}_t$ from inside the body is $\rho_1^-\psi_1^-(\mathbf{v}_1^- - \mathbf{V})\cdot\mathbf{n} + \rho_2^-\psi_2^-(\mathbf{v}_2^- - \mathbf{V})\cdot\mathbf{n}$ per unit area per unit time. The net outflow of energy away from $\partial\mathcal{R}_t$ into the outside of the body is $\rho_2^+\psi_2^+(\mathbf{v}_2^+ - \mathbf{V})\cdot\mathbf{n}$ keeping in mind that there are no species-1 particles outside the body. The increase in free energy, i.e. the difference between the free energy outflow and inflow, is therefore

$$\Delta E = \Big(\rho_2^+\psi_2^+(\mathbf{v}_2^+ - \mathbf{V})\cdot\mathbf{n}\Big) - \Big(\rho_1^-\psi_1^-(\mathbf{v}_1^- - \mathbf{V})\cdot\mathbf{n} + \rho_2^-\psi_2^-(\mathbf{v}_2^- - \mathbf{V})\cdot\mathbf{n}\Big). \tag{3.14}$$

An alternative interpretation of (3.14) at a point where dissociation occurs can be inferred by first using mass balance (3.8) to eliminate the term $\rho_2^+(\mathbf{v}_2^+ - \mathbf{V})$ leading to the equivalent expression

$$\Delta E = (\psi_2^+ - \psi_1^-)\rho_1^-(\mathbf{v}_1^- - \mathbf{V})\cdot\mathbf{n} \;+\; (\psi_2^+ - \psi_2^-)\rho_2^-(\mathbf{v}_2^- - \mathbf{V})\cdot\mathbf{n}. \tag{3.15}$$

The mass of species-1 material that arrives at $\partial\mathcal{R}_t$ from the interior, i.e. $\rho_1^-(\mathbf{v}_1^- - \mathbf{V})\cdot\mathbf{n}$, transforms into species-2 and so changes its free energy from ψ_1^- to ψ_2^+ as it exits the body. This corresponds to the first term in (3.15). Similarly the species-2 material arriving at $\partial\mathcal{R}_t$ from the interior changes its free energy from ψ_2^- to ψ_2^+ as it diffuses out of the body (continuing to remain as species-2). This is described by the second term.

Next consider a point on $\partial\mathcal{R}_t$ at which association occurs. Using mass balance (3.8) to eliminate the term $\rho_1^-(\mathbf{v}_1^- - \mathbf{V})$ from (3.14) leads to the alternative expression

$$\Delta E = (\psi_1^- - \psi_2^+)\rho_2^+(\mathbf{V} - \mathbf{v}_2^+)\cdot\mathbf{n} \;+\; (\psi_1^- - \psi_2^-)\rho_2^-(\mathbf{v}_2^- - \mathbf{V})\cdot\mathbf{n}. \tag{3.16}$$

The species-2 material arriving at $\partial\mathcal{R}_t$ from outside the body transforms into species-1 and so changes its free energy from ψ_2^+ to ψ_1^- as described by the first term above. Similarly the species-2 material arriving at $\partial\mathcal{R}_t$ from the interior transforms into species-1 and so changes its free energy from ψ_2^- to ψ_1^- as described by the second term.

We shall also allow for the possibility that the chemical reaction taking place on the boundary of the body due to the transformation of one species into the other requires some additional amount of energy. We describe this by an energy source ψ_r (per unit mass). The rate at which species-2 is transformed into species-1, i.e. the rate at which solid material is added to the body, is $\rho_{R1} V_R \, dA_x$ (mass per unit time) and so the associated energy is $\rho_{R1}\psi_r V_R \, dA_x$. In view of (3.7) this can be written as

$$\rho_1^- \, \psi_r \, (\mathbf{V} - \mathbf{v}_1^-) \cdot \mathbf{n} \, dA_y. \tag{3.17}$$

It should be noted that the energy ψ_r corresponding to association may be different to that corresponding to dissociation. Thus

$$\psi_r = \begin{cases} \psi_a & \text{for } V_R > 0, \\ \psi_d & \text{for } V_R < 0, \end{cases} \tag{3.18}$$

where ψ_a and ψ_d are the respective energies per unit mass that are added to the body by the association and dissociation chemical reactions.

Finally the rate of working of the tractions on $\partial\mathcal{R}_t$ is

$$\mathbf{T}_2^+ \mathbf{n} \cdot \mathbf{v}_2^+ + \mathbf{T}_1^- (-\mathbf{n}) \cdot \mathbf{v}_1^- + \mathbf{T}_2^- (-\mathbf{n}) \cdot \mathbf{v}_2^- . \tag{3.19}$$

The *dissipation rate due to growth* is found by adding (3.19) and (3.17) and subtracting (3.14) from the result:

$$\begin{aligned} \mathbb{D} = \int_{\partial\mathcal{R}_t} \Big[& \Big(\mathbf{T}_2^+ \mathbf{n} \cdot \mathbf{v}_2^+ - \mathbf{T}_1^- \mathbf{n} \cdot \mathbf{v}_1^- - \mathbf{T}_2^- \mathbf{n} \cdot \mathbf{v}_2^- \Big) \; + \; \rho_1^- \psi_r (\mathbf{V} - \mathbf{v}_1^-) \cdot \mathbf{n} \; - \\ & - \Big(\rho_2^+ \psi_2^+ (\mathbf{v}_2^+ - \mathbf{V}) \cdot \mathbf{n} - \rho_1^- \psi_1^- (\mathbf{v}_1^- - \mathbf{V}) \cdot \mathbf{n} - \rho_2^- \psi_2^- (\mathbf{v}_2^- - \mathbf{V}) \cdot \mathbf{n} \Big) \Big] \, dA_y. \end{aligned} \tag{3.20}$$

Note from (2.43) that the stress in the fluid outside the body is

$$\mathbf{T}^+ = \mathbf{T}_2^+ = -p^+ \mathbf{I} \qquad \text{where} \qquad p^+ := -\rho_2^+ (\psi_2^+ - \mu). \tag{3.21}$$

By traction and chemical potential continuity across $\partial\mathcal{R}_t$, together with the constitutive relations $\mathbf{T}_2^+ = \rho_2^+ (\psi_2^+ - \mu)\mathbf{I}$ and $\mathbf{T}_2^- = \rho_2^- (\psi_2^- - \mu)\mathbf{I}$, and the mass balance equation (3.8), one can simplify (3.20) to obtain

$$\mathbb{D} = \int_{\partial\mathcal{R}_t} \Big[- p^+ - \rho^- (\psi^- - \mu) + \rho_1^- \psi_r \Big] \, (\mathbf{V} - \mathbf{v}_1^-) \cdot \mathbf{n} \, dA_y. \tag{3.22}$$

This can be written in referential form by using (3.6) as

$$\mathbb{D} = \int_{\partial\mathcal{R}_{R1}} \Big[- p^+ - \rho^- (\psi^- - \mu) + \rho_1^- \psi_r \Big] \, J_1^- \, V_R \, dA_x \;=\; \int_{\partial\mathcal{R}_{R1}} f V_R \, dV_x, \tag{3.23}$$

where

$$f := -p^+ J_1^- - (\varphi^- - \rho^- J_1^- \mu) + \rho_{R1}\, \psi_r \qquad \text{on } \partial\mathcal{R}_{R1}, \tag{3.24}$$

is the *driving force* f *associated with growth.* The dissipation inequality requires

$$f\, V_R \geq 0 \qquad \text{on } \partial\mathcal{R}_{R1}.$$

According to $(3.23)_2$ the growth rate V_R is conjugate to the driving force f and so we assume that the kinetics of growth is characterize by a kinetic law

$$V_R = \mathcal{V}(f), \tag{3.25}$$

where $\mathcal{V}(f)f \geq 0$. If $\mathcal{V}(\cdot)$ is a monotonically increasing function with $\mathcal{V}(0) = 0$, association ($V_R > 0$) corresponds to $f > 0$ while disssociation ($V_R < 0$) corresponds to $f < 0$:

$$\text{Association} : f > 0, \qquad \text{Dissociation} : f < 0. \tag{3.26}$$

Before ending this section we outline an alternative derivation of the preceding expressions for the dissipation rate and driving force. The total dissipation rate associated with the body (including bulk dissipation) is described by

$$\mathbb{D}_{\text{total}} = \int_{\partial\mathcal{R}_t} \mathbf{T}^+\mathbf{n}\cdot\mathbf{V}\, dA_y + \int_{\partial\mathcal{R}_t} -\mu\mathbf{h}^+\cdot\mathbf{n}\, dA_y + \int_{\partial\mathcal{R}_t} \rho_1\, \psi_r\, (\mathbf{V}-\mathbf{v}_1)\cdot\mathbf{n}\, dA_y - \frac{d}{dt}\int_{\mathcal{R}_t} \rho\psi\, dV_y. \tag{3.27}$$

The first term represents the rate of external working on the body, the second is the influx of chemical potential into the body across its moving boundary, and the third term accounts for the chemical reaction taking place on the boundary of the body. Note that since the region $\mathcal{R}_t$ is not material with respect to either species, it is the velocity $\mathbf{V}$ of the boundary and the flux $\mathbf{h}$ across the moving boundary that enter (3.27). This can be compared (and contrasted) with (2.47) where there, the region D_1 was material with respect to species-1 and so the velocity of the boundary was $\mathbf{v}_1$ and the flux was the flux $\mathbf{j}$ of species-2 across a material surface.

By using the transport theorem together with (2.41), (3.6), $(2.43)_1$, (2.44), $\dot{\mathbf{F}}_1 = \mathbf{L}_1\mathbf{F}_1$, (2.5), (2.14), (2.38) and the divergence theorem one can show that

$$\frac{d}{dt}\int_{\mathcal{R}_t} \rho\psi \, dV_y = \int_{\mathcal{R}_t} -\mu \, \mathrm{div}\, \mathbf{j} \; dV_y + \int_{\partial\mathcal{R}_t} \Big[\mathbf{T}^{-}\mathbf{n}\cdot\mathbf{v}_1^{-} + \rho^{-}\psi^{-}\,(\mathbf{V}-\mathbf{v}_1^{-})\cdot\mathbf{n}\Big] dA_y. \tag{3.28}$$

Equation (3.27) can now be simplified by using (3.28) and the divergence theorem, together with traction continuity, (3.12), (3.10), (2.9) and $(2.6)_1$ leading to

$$\mathbb{D}_{\text{total}} = \int_{\partial\mathcal{R}_t} \Big[\mathbf{T}^{-} - \rho^{-}(\psi^{-}-\mu)\mathbf{I} + \rho_1^{-}\psi_r\mathbf{I}\Big]\mathbf{n}\cdot\ (\mathbf{V}-\mathbf{v}_1)\, dA_y - \int_{\mathcal{R}_t} \mathbf{j}\cdot \mathrm{grad}\,\mu\, dV_y. \tag{3.29}$$

Finally, this can be further simplified by using traction continuity $\mathbf{T}^{-}\mathbf{n} = \mathbf{T}_2^{+}\mathbf{n}$ once more together and (3.21), to obtain

$$\mathbb{D}_{\text{total}} = \mathbb{D}\ - \int_{\mathcal{R}_t} \mathbf{j}\cdot\mathrm{grad}\,\mu\, dV_y, \tag{3.30}$$

where $\mathbb{D}$ coincides with the expression (3.22) derived previously for the dissipation rate due to growth.

4 Growth on a fixed impermeable rigid surface.

In the preceding section we assumed that the body was completely surrounded by a reservoir of species-2 (the fluid). There are settings where growth (usually association) takes place at a fixed rigid, impermeable surface, say Σ. In this case the body is in contact with Σ and there are no particles of either species on the outer side of this surface. Since Σ is fixed in physical space, it follows that

$$\mathbf{V} = \mathbf{0}, \tag{4.1}$$

and therefore from (3.2) that

$$\mathbf{v}_1 = -V_R\mathbf{F}_1\mathbf{n}_R. \tag{4.2}$$

First consider mass balance. Equations (3.8) and (3.9) continue to hold with $\rho_2^{+} = 0$ and $\mathbf{V} = \mathbf{0}$, so that in particular

$$\mathbf{j}^{-}\cdot\mathbf{n} + \rho^{-}\mathbf{v}_1^{-}\cdot\mathbf{n} = 0 \qquad \text{on } \Sigma. \tag{4.3}$$

We remark again that while this equation is correct, $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$ represents the flux (of species-2) across a surface that is material with respect to species-1, and Σ is not such a surface.

We now turn to the dissipation rate at Σ. Since $\mathbf{V} = \mathbf{0}$, the inflow of free energy per unit area per unit time *into* Σ from inside the body is $\rho_1^- \psi_1^- \mathbf{v}_1^- \cdot \mathbf{n} + \rho_2^- \psi_2^- \mathbf{v}_2^- \cdot \mathbf{n}$. There is no outflow of energy into the outer side of Σ. Thus the difference between the outflow and inflow of energy at Σ

$$= -\Big(\rho_1^- \psi_1^- \mathbf{v}_1^- \cdot \mathbf{n} + \rho_2^- \psi_2^- \mathbf{v}_2^- \cdot \mathbf{n}\Big) = -\rho^- \psi^- \mathbf{v}_1^- \cdot \mathbf{n} - \psi_2^- \mathbf{j}^- \cdot \mathbf{n}, \tag{4.4}$$

where we have used $\rho\psi = \rho_1\psi_1 + \rho_2\psi_2$ and $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$ in getting to the second equality. Since there are no particles outside Σ the rate of working (per unit area) by the traction on Σ

$$= \mathbf{T}_1^-(-\mathbf{n}) \cdot \mathbf{v}_1^- + \mathbf{T}_2^-(-\mathbf{n}) \cdot \mathbf{v}_2^- = -\mathbf{T}^-\mathbf{n} \cdot \mathbf{v}_1^- - (\psi_2^- - \mu)\,\mathbf{j}^- \cdot \mathbf{n}, \tag{4.5}$$

having used $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2, \mathbf{T}_2 = \rho_2(\psi_2 - \mu)\mathbf{I}$ and $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$ in the second step.

Therefore the *dissipation rate* at the surface Σ is found by adding the chemical reaction energy term $-\rho_1^- \psi_r \mathbf{v}_1^- \cdot \mathbf{n}$ to (4.5) and subtracting (4.4) from the result leading to

$$\mathbb{D}_\Sigma = \int_\Sigma \Big[(\rho^- \psi^- - \rho_1^- \psi_r)\mathbf{v}_1^- \cdot \mathbf{n} + \mu \mathbf{j}^- \cdot \mathbf{n} - \mathbf{T}^-\mathbf{n} \cdot \mathbf{v}_1^-\Big]\, dA_y. \tag{4.6}$$

The parameter ψ_r is chosen according to (3.18). The flux $\mathbf{j}^-$ can be eliminated by using the mass balance condition (4.3) which leads to

$$\mathbb{D}_\Sigma = \int_\Sigma \Big[- \mathbf{T}^- + \big[\rho^-(\psi^- - \mu) - \rho_1^- \psi_r\big]\mathbf{I}\Big]\mathbf{v}_1^- \cdot \mathbf{n}\, dA_y. \tag{4.7}$$

Observe that the integrand here coincides with the integrand of the surface integral term in (3.29) with $\mathbf{V} = \mathbf{0}$. Finally on using (4.2) and (3.1) we have the referential form

$$\mathbb{D}_\Sigma = \int_{\Sigma_R} \Big[\mathbf{S}^-\mathbf{n}_R \cdot \mathbf{F}_1^-\mathbf{n}_R - \rho^- J_1^-(\psi^- - \mu) + \rho_{R1}\psi_r\Big]\, V_R\, dA_x, \tag{4.8}$$

where Σ_R is the image of Σ in the reference configuration and

$$\mathbf{S}^- = J_1^- \mathbf{T}^- \mathbf{F}_1^{-\,-T}. \tag{4.9}$$

The *driving force on the fixed surface* Σ is therefore

$$f \;:=\; \mathbf{S}^-\mathbf{n}_R \cdot \mathbf{F}_1^-\mathbf{n}_R - (\varphi^- - \rho^- J_1^- \mu) + \rho_{R1}\psi_r \qquad \text{on } \Sigma_R, \tag{4.10}$$

where $\varphi = \rho\psi J_1$. The dissipation inequality requires

$$fV_R \geq 0 \qquad \text{on } \Sigma_R.$$

4.1 More kinematics.

Suppose that the reason growth takes place at the support surface Σ is because it has been treated with a certain chemical that attracts the monomers, and suppose further that this chemical treatment creates a distribution of binding sites on Σ to which the growing polymer chains attach. These sites are assumed to occur at fixed locations on Σ and so the tangential deformation of the polymer, parallel to the support surface, is predetermined. Suppose that this corresponds to a prescribed two-dimensional isotropic stretch λ_0 parallel to Σ. Based on this we require that, at each point on Σ, $\mathbf{F}_1\boldsymbol{\ell} = \lambda_0\boldsymbol{\ell}$ for all unit vectors $\boldsymbol{\ell}$ perpendicular to $\mathbf{n}_R$. This implies that $\mathbf{F}_1$ can be expressed as

$$\mathbf{F}_1 = \lambda_0\mathbf{I} + \mathbf{a}\otimes\mathbf{n}_R \qquad \text{on } \Sigma_R, \tag{4.11}$$

for some arbitrary (possibly $\mathbf{x}$ and t-dependent) vector $\mathbf{a}$. For this $\mathbf{F}_1$,

$$J_1 = \det\mathbf{F}_1 = \lambda_0^2(\lambda_0 + \mathbf{a}\cdot\mathbf{n}_R), \qquad \mathbf{F}_1^{-1} = \lambda_0^{-1}\left[\mathbf{I} - \frac{\lambda_0^2}{J_1}\mathbf{a}\otimes\mathbf{n}_R\right] \qquad \text{on } \Sigma_R. \tag{4.12}$$

On using this in the relation (3.1) between area elements in the current and reference configurations, one finds (as one would expect) that

$$dA_y = \lambda_0^2\, dA_x, \qquad \mathbf{n} = \mathbf{n}_R \qquad \text{on } \Sigma_R. \tag{4.13}$$

The particle velocity (4.2) at the growth surface can now be simplified using (6.65) and $(6.67)_2$ to read

$$\mathbf{v}_1 = -\lambda_0 V_R\mathbf{n} - V_R\mathbf{a} \qquad \text{on } \Sigma. \tag{4.14}$$

Assume that the growth velocity $\mathbf{V}_G$ defined previously in (3.3) is normal to the growth surface. However, in view of (4.1) and (3.3), in the present setting the growth velocity equals the particle velocity because the surface Σ is fixed. Consequently the particle velocity $\mathbf{v}_1$ must also be normal to Σ and therefore $\mathbf{a}$ must be parallel to $\mathbf{n}$. So we may write

$$\mathbf{a} = (\lambda - \lambda_0)\mathbf{n},$$

for some scalar λ whence

$$\mathbf{F}_1 = \lambda\,\mathbf{n}_R\otimes\mathbf{n}_R + \lambda_0(\mathbf{I} - \mathbf{n}_R\otimes\mathbf{n}_R), \qquad J_1 = \lambda\lambda_0^2 \qquad \text{on } \Sigma_R, \tag{4.15}$$

having used $(6.67)_2$. Thus λ represents the stretch normal to Σ (while λ_0 is the tangential stretch). The particle velocity at the growth surface given by (6.68) now reduces to

$$\mathbf{v}_1 = -\lambda V_R\,\mathbf{n} \qquad \text{on } \Sigma. \tag{4.16}$$

Observe that if there is no growth, $V_R = 0$, whence $\mathbf{v}_1 = \mathbf{0}$.

4.2 Driving force (continued).

It now follows from (6.69) that

$$\mathbf{F}_1\mathbf{n}_R = \lambda\mathbf{n}_R,$$

and from (4.9) and (6.69) that

$$\mathbf{S}^-\mathbf{n}_R = \lambda_0^2\,\mathbf{T}^-\mathbf{n}.$$

The driving force for growth (4.10) now specializes to

$$f \;=\; J_1\mathbf{T}^-\mathbf{n}\cdot\mathbf{n} - (\varphi^- - \rho^- J_1^-\mu) + \rho_{R1}\psi_r \qquad \text{on } \Sigma_R, \tag{4.17}$$

Observe that this expression coincides with the expression (3.24) for the driving force at a free growth surface provided we set $p^+ = -\mathbf{T}^-\mathbf{n}\cdot\mathbf{n}$.

5 SUMMARY

with subscript 1 dropped from the kinematic quantities $\mathbf{v}_1, \mathbf{F}_1, J_1$ and the derivative D_1/Dt. Also the superscript $-$ is dropped

Field equations (recall $c_R = \rho_2 J_1$ and $\varphi = \rho\psi J$)

$$\mathbf{div}\,\mathbf{T} = \mathbf{0} \tag{5.1}$$

$$\frac{1}{J}\frac{Dc_R}{Dt} + \operatorname{div}\mathbf{j} = 0. \tag{5.2}$$

$$\mathbf{j} = -m\,\rho_2\,\operatorname{grad}\mu = -m\,\frac{c_R}{1+\nu c_R}\operatorname{grad}\mu \tag{5.3}$$

$$J = 1 + \nu c_R. \tag{5.4}$$

$$\mathbf{T} = \frac{1}{J}\frac{\partial\varphi}{\partial\mathbf{F}}\mathbf{F}^T - q\,\mathbf{I}. \tag{5.5}$$

$$\mu = \frac{\partial\varphi}{\partial c_R} + \nu q, \tag{5.6}$$

$$m \geq 0. \tag{5.7}$$

Recall $\varphi = \rho\psi J$ and

$$\rho = \frac{\rho_{R1} + c_R}{1+\nu c_R} = \frac{\rho_{R1} + c_R}{J}. \tag{5.8}$$

Boundary conditions: When body is completely surrounded by a bath of species-2:

$$\mathbf{Tn} = -p_0\mathbf{n} \qquad \text{where } p_0 \text{ is given.} \tag{5.9}$$

$$\mu = \mu_\infty \tag{5.10}$$

$$V_R = \mathcal{V}(f) \tag{5.11}$$

where

$$f = -p^+J - \varphi + \rho J\mu + \rho_{R1}\psi_r \tag{5.12}$$

and ψ_r is chosen according to

$$\psi_r = \begin{cases} \psi_a & \text{for } f > 0, \\ \psi_d & \text{for } f < 0. \end{cases} \tag{5.13}$$

When body is partially surrounded by a bath of species-2, the same conditions as above hold on that part of the boundary that is in contact with the bath.

When part of the boundary is a fixed rigid surface:

$$\mathbf{v} = -V_R\mathbf{F}_1\mathbf{n}_R, \tag{5.14}$$

$$\mathbf{j}\cdot\mathbf{n}+\rho\mathbf{v}\cdot\mathbf{n}=0 \tag{5.15}$$

$$V_R=\mathcal{V}(f) \tag{5.16}$$

where

$$f=\mathbf{S}\mathbf{n}_R\cdot\mathbf{F}\mathbf{n}_R-\varphi+\rho J\mu+\rho_{R1}\psi_r \tag{5.17}$$

and ψ_r is chosen as above.

$$\nu=1/\rho_{R2} \tag{5.18}$$

$$\rho J=\rho_{R1}+c_R \tag{5.19}$$

6 Prolem 1: Growth on a flat rigid impermeable plate

We now apply the preceding theory to the particular problem of growth on an infinite, rigid, impermeable, flat substrate. Choose y_1, y_2, y_3-axes with the plane $y_1 = 0$ corresponding to the growth surface. At time t, the slab-like body occupies a region $0 \le y_1 \le \ell(t),\ -\infty < y_2, y_3 < \infty$. In the reference configuration the body occupies a region $Z_a(t) \le x_1 \le Z_d(t),\ -\infty < x_2, x_3 < \infty$. In this setting the respective velocities of the boundaries of the body in the current and reference configurations are

$$\mathbf{V} = \mathbf{0} \quad \text{on } y_1 = 0, \qquad \mathbf{V} = \dot{\ell}\,\mathbf{e}_1 \quad \text{on } y_1 = \ell(t), \tag{6.1}$$

and

$$\mathbf{V}_R = \dot{Z}_a \mathbf{e}_1 \quad \text{on } x_1 = Z_a(t), \qquad \mathbf{V}_R = \dot{Z}_d \mathbf{e}_1 \quad \text{on } x_1 = Z_d(t), \tag{6.2}$$

where $\mathbf{e}_1$ is a unit vector in the y_1-direction. We can write (6.2) as

$$\mathbf{V}_R = V_R \mathbf{n}_R \qquad \text{where} \qquad V_R = \begin{cases} -\dot{Z}_a & \text{on } x_1 = Z_a(t), \\ \dot{Z}_d & \text{on } x_1 = Z_d(t), \end{cases} \tag{6.3}$$

since the respective unit outward normal vectors on $x_1 = Z_a(t)$ and $x_1 = Z_d(t)$ are $\mathbf{n}_R = -\mathbf{e}_1$ and $\mathbf{n}_R = \mathbf{e}_1$. The thickness of the slab in the reference configuration is

$$\ell_R(t) = Z_d(t) - Z_a(t). \tag{6.4}$$

Any change in the dimension ℓ_R is due to growth, whereas the dimension ℓ changes due to both growth and "swelling" (i.e. change of solvent content).

A certain (known) distribution of binding sites on the substrate causes the material to be stretched[6] by a constant amount λ_0 equibiaxially parallel to the growth surface when it is deposited. It is convenient to let $x = x_1$ and $y = y_1$. Therefore the deformation that maps $(x, x_2, x_3) \to (y, y_2, y_3)$ is

$$\mathbf{y}(\mathbf{x}, t) = y(x,t)\,\mathbf{e}_1 + \lambda_0 x_2\,\mathbf{e}_2 + \lambda_0 x_3\,\mathbf{e}_3, \tag{6.5}$$

and the associated particle velocity, deformation gradient tensor, stretch and Jacobian determinant are

$$\mathbf{v} = v\,\mathbf{e}_1 \qquad \text{where } v = \frac{\partial y}{\partial t}(x,t), \tag{6.6}$$

$$\mathbf{F} = \lambda\,\mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_0\,\mathbf{e}_2 \otimes \mathbf{e}_2 + \lambda_0\,\mathbf{e}_3 \otimes \mathbf{e}_3 \qquad \text{where } \lambda = \frac{\partial y}{\partial x}(x,t), \tag{6.7}$$

$$J = \det \mathbf{F} = \lambda \lambda_0^2. \tag{6.8}$$

In view of the kinematic constraint $J = 1 + \nu c_R$, the stretch λ is related to the monomer concentration c_R by

$$\lambda = \widehat{\lambda}(c_R) := \lambda_0^{-2}(1 + \nu\, c_R). \tag{6.9}$$

An important remark is that we can use (6.9) to convert any function of λ into a function of c_R and vice versa.

[6] relative to the reference configuration associated with the dry solid

We next calculate the particle velocities at the two boundaries by differentiating

$$0 = y(Z_a(t), t), \qquad \ell(t) = y(Z_d(t), t),$$

with respect to time. This leads to

$$v = -\lambda \dot{Z}_a \qquad \text{on } y = 0, \qquad v = \dot{\ell} - \lambda \dot{Z}_d \qquad \text{on } y = \ell. \tag{6.10}$$

These particle velocities can be expressed in terms of the concentration c_R (and t) using (6.9):

$$v = -\lambda_0^{-2}(1 + \nu c_R)\, \dot{Z}_a \quad \text{on } x = Z_a(t), \qquad v = \dot{\ell} - \lambda_0^{-2}(1 + \nu c_R)\, \dot{Z}_d \quad \text{on } x = Z_d(t). \tag{6.11}$$

These are the specialzation of (3.2) to the present setting.

Turning now to the constitutive relation for the free energy, since it has the form $\rho\psi(\mathbf{F}_1, \rho_2) = \rho_1\psi_1(\mathbf{F}_1, \rho_2) + \rho_2\psi_2(\mathbf{F}_1, \rho_2)$ we can write

$$\varphi = \rho_{R1}\psi_1(\mathbf{F}_1, \rho_2) + c_R\psi_2(\mathbf{F}_1, \rho_2) = \overline{\psi}_1(\mathbf{F}, c_R) + \overline{\psi}_2(\mathbf{F}, c_R),$$

having used $\varphi = \rho J_1 \psi, \rho_1 J_1 = \rho_{R1}, c_R = \rho_2 J_1$ and dropped the subscript 1. We follow the classical Frenkel-Flory-Rehner approach and assume that the elastic energy is carried solely by species-1 (the polymer network), while the energy of mixing is carried by species-2 (the monomers) and so we write

$$\varphi(\mathbf{F}, c_R) = \overline{W}(\lambda_1, \lambda_2, \lambda_3) + \widehat{\varphi}_s(c_R) + \mu_\infty c_R, \tag{6.12}$$

having assumed isotropy. Here $\overline{W}$ represents the elastic energy (associated with the deformation of the polymer network), $\widehat{\varphi}_s$ is the mixing energy of the solvent, and the λ's are the principal stretches. Explicit expressions for $\overline{W}$ and $\widehat{\varphi}_s$ will be given later when we make specific constitutive choices.

The constitutive relation (5.5) for stress is readily seen to yield

$$T_{11} = \lambda_0^{-2} W'(\lambda) - q \tag{6.13}$$

where W is defined by

$$W(\lambda) := \overline{W}(\lambda, \lambda_0, \lambda_0). \tag{6.14}$$

The energies W and φ can be expressed in terms of the solvent concentration c_R by using (6.9):

$$\widehat{W}(c_R) := W(\widehat{\lambda}(c_R)) = W(\lambda_0^{-2}(1 + \nu c_R)), \qquad \widehat{\varphi}(c_R) = \widehat{W}(c_R) + \widehat{\varphi}_s(c_R) + \mu_\infty c_R. \tag{6.15}$$

A word on notation: in this section we will be able to express various quantities of interest in terms of c_R and we shall use a hat "$\widehat{\ }$" to denote such functions, e.g. $\widehat{W}(c_R), \widehat{\mu}(c_R), \widehat{f}(c_R), \widehat{V}_a(c_R)$, etc.

As for the prescribed boundary conditions on $y = \ell(t)$, we assume that a constant normal Cauchy pressure p_0 is applied on this surface and that it is at a constant chemical potential μ_∞ by virtue of being in contact with a large reservoir of monomers.

The equilibrium equation $\operatorname{div}\mathbf{T} = \mathbf{0}$ specializes in the current setting to

$$\frac{\partial T_{11}}{\partial y} = 0 \qquad \text{for } 0 \le y \le \ell(t). \tag{6.16}$$

Integrating this and using the boundary condition $T_{11} = -p_0$ at $y = \ell$ yields

$$T_{11}(y,t) = -p_0 \qquad \text{for } 0 \le y \le \ell(t).$$

Combining this with (6.13) gives the following expression for the constraint pressure q:

$$q = \widehat{q}(c_R) := \lambda_0^{-2} W'(\lambda)\Big|_{\lambda=\widehat{\lambda}(c_R)} + p_0 = \nu^{-1}\widehat{W}'(c_R) + p_0. \tag{6.17}$$

The chemical potential is given by (5.6), (6.12) to be

$$\mu = \widehat{\varphi}_s'(c_R) + \mu_\infty + \nu q, \tag{6.18}$$

so that eliminating q using (6.17) leads to the following expression for the chemical potential in terms of the monomer concentration:

$$\mu = \widehat{\mu}(c_R) := \widehat{\varphi}'(c_R) + \nu p_0. \tag{6.19}$$

Next consider the monomer flux $\mathbf{j} = j\,\mathbf{e}_1$. From (5.3), $(6.7)_2$, (6.8) and (6.9) we have

$$j = -m\frac{c_R}{1+\nu c_R}\frac{\partial \mu}{\partial y} = -m\frac{c_R}{(1+\nu c_R)\lambda}\,\widehat{\mu}'(c_R)\frac{\partial c_R}{\partial x} = -m\frac{c_R\lambda_0^2}{(1+\nu c_R)^2}\,\widehat{\mu}'(c_R)\frac{\partial c_R}{\partial x}, \tag{6.20}$$

and so this flux can be written as

$$j = -\lambda_0^{-2}\, D(c_R)\frac{\partial c_R}{\partial x}, \tag{6.21}$$

where we have set

$$D(c_R) := -m\frac{c_R\lambda_0^4}{(1+\nu c_R)^2}\,\widehat{\mu}'(c_R). \tag{6.22}$$

Turning to the solvent diffusion field equation (5.2) we note that it reduces in the present setting to

$$0 = \dot{c}_R + J\frac{\partial j}{\partial y} = \dot{c}_R + \frac{J}{\lambda}\frac{\partial j}{\partial x} = \dot{c}_R + \lambda_0^2\frac{\partial j}{\partial x}, \tag{6.23}$$

having used (6.8). Combining this with (6.21) leads to

$$\dot{c}_R = \frac{\partial}{\partial x}\left(D(c_R)\frac{\partial c_R}{\partial x}\right). \tag{6.24}$$

This is a differential equation for the referential monomer concentration $c_R(x,t)$.

We now turn to the boundary conditions at the association surface $y = 0$. Here we must enforce (5.15) which balances the flux of monomers reaching $y = 0$ with the rate at which they are converted into polymer molecules. In the present problem this boundary condition (5.15) specializes to $j + \rho v = 0$ from which the particle velocity can be eliminated using $(6.10)_1$ leading to

$$j = \rho\lambda\dot{Z}_a \qquad \text{for } x = Z_a(t). \tag{6.25}$$

Finally, combining this with (6.21) gives the following boundary condition on the concentration gradient at the association surface:

$$D(c_a)\frac{\partial c_R}{\partial x} = -(\rho_{R1} + c_a)\,\dot{Z}_a \qquad \text{for } x = Z_a(t), \tag{6.26}$$

where we have also used (5.8), (6.3) and (6.8). We have denoted the monomer concentration at the association surface by $c_a(t)$:

$$c_a(t) \coloneqq c_R(Z_a(t), t). \tag{6.27}$$

We turn next to the chemical boundary condition at the dissociation surface $y = \ell$ which is assumed to be at a known chemical potential μ_∞. Since the chemical potential is required to be continuous, it follows that $\mu(\ell(t), t) = \mu_\infty$, and therefore by (6.19) that

$$\widehat{\mu}(c_R) = \mu_\infty \qquad \text{at } x = Z_d(t). \tag{6.28}$$

Thus the monomer concentration at the dissociation surface,

$$c_d \coloneqq c_R(Z_d(t), t), \tag{6.29}$$

has a *time independent* constant value c_d given by the root(s) of

$$\widehat{\mu}(c_d) = \mu_\infty. \tag{6.30}$$

We need two more equations to find $Z_a(t)$ and $Z_d(t)$ and these are given by the kinetic relations. At the association surface, we specialize the general expression (4.10) for the driving force to the present setting to obtain

$$f_a = -p_0\lambda_0^2\lambda - \varphi + \rho\mu J + \rho_{R1}\psi_a. \tag{6.31}$$

This can be written in terms of the monomer concentration c_a by using (5.4), (5.8), $(6.15)_2$ and (6.19):

$$f_a = \widehat{f}_a(c_a) \coloneqq -p_0(1 + \nu c_a) - \widehat{\varphi}(c_a) + \widehat{\mu}(c_a)(\rho_{R1} + c_a) + \rho_{R1}\psi_a. \tag{6.32}$$

Similarly at the dissociation surface we specialize (3.24) to obtain

$$f_d = -p_0 J - \varphi + \rho\mu J + \rho_{R1}\psi_d, \tag{6.33}$$

which can be written in terms of the monomer concentration c_d as

$$f_d = \widehat{f}_d(c_d) \coloneqq -p_0(1 + \nu c_d) - \widehat{\varphi}(c_d) + \widehat{\mu}(c_d)(\rho_{R1} + c_d) + \rho_{R1}\psi_d. \tag{6.34}$$

Observe that the only difference between the functions $\widehat{f}_a$ and $\widehat{f}_d$ is in the additive constant terms $\rho_{R1}\psi_a$ and $\rho_{R1}\psi_d$. Thus the kinetic relations (5.11) at the association and dissociation surfaces yield

$$-\dot{Z}_a = \widehat{V}_a(c_a) \coloneqq \mathcal{V}_a(\widehat{f}_a(c_a)), \qquad \dot{Z}_d = \widehat{V}_d(c_d) \coloneqq \mathcal{V}_d(\widehat{f}_d(c_d)). \tag{6.35}$$

In summary, from (6.24), (6.26) and (6.29) we have

$$\left.\begin{array}{rcll} \dot{c}_R &=& \dfrac{\partial}{\partial x}\left(D(c_R)\dfrac{\partial c_R}{\partial x}\right) & \text{for } Z_a(t) < x < Z_d(t), \\ D(c_a)\dfrac{\partial c_R}{\partial x} &=& (\rho_{R1} + c_a)\,\widehat{V}_a(c_a) & \text{on } x = Z_a(t), \\ c_R &=& c_d & \text{on } x = Z_d(t), \end{array}\right\} \tag{6.36}$$

where c_d is given by (6.30) and $c_a(t) = c_R(Z_a(t), t)$. This boundary value problem is supplemented by

$$-\dot{Z}_a(t) = \widehat{V}_a\big(c_a(t)\big), \qquad \dot{Z}_d = \widehat{V}_d(c_d), \tag{6.37}$$

and appropriate initial conditions. Since c_d is time independent, so is the association rate $\dot{Z}_d$.

The problem has therefore been reduced to one that involves the unknowns $c_R(x,t), Z_a(t)$ and $Z_d(t)$. They are governed by the differential equation $(6.36)_1$, the two associated boundary conditions $(6.36)_{2,3}$, and the kinetic relations (6.37) .

6.1 Solution: case of slow growth.

If growth occurs much more slowly than monomer diffusion through the solid, we may omit the term $\dot{c}_R$ from $(6.36)_1$. Integrating the resulting equation with respect to x and using the boundary condition $(6.36)_2$ yields

$$D(c_R)\frac{\partial c_R}{\partial x} = (\rho_{R1} + c_a)\,\widehat{V}_a(c_a) \qquad \text{for } Z_a(t) < x < Z_d(t). \tag{6.38}$$

Integrating again with respect to x and using $(6.36)_3$ yields

$$-(\rho_{R1} + c_a)\,\widehat{V}_a(c_a)(Z_d - x) = \int_{c_R}^{c_d} D(\xi)\,d\xi \qquad \text{for } Z_a(t) < x < Z_d(t). \tag{6.39}$$

Setting $x = Z_a$ and $\ell_R = Z_d - Z_a$ in here yields

$$\ell_R = \frac{1}{(\rho_{R1} + c_a)\,\widehat{V}_a(c_a)} \int_{c_d}^{c_a} D(c_R)\,dc_R. \tag{6.40}$$

Recall that ℓ_R is the thickness of the slab in the reference configuration. This, together with

$$\dot{\ell}_R = \widehat{V}_d(c_d) + \widehat{V}_a(c_a) \tag{6.41}$$

(which follows from (6.4) and (6.37)), and suitable initial conditions constitutes the initial value problem for $\ell_R(t)$. Once $\ell_R(t)$ is thus found, (6.40) gives $c_a(t)$ and then (6.39) gives $c_R(x,t)$ provided the relevant functions associated with these equations are invertible. All other fields can then be readily found.

Special case: treadmilling. In a treadmilling state, by definition, the referential thickness of the slab, ℓ_R, is constant and so in view of (6.4),

$$\dot{Z}_d = \dot{Z}_a.$$

Therefore from (6.37)

$$\widehat{V_a}(c_a) = -\widehat{V_d}(c_d). \tag{6.42}$$

Given μ_∞ we solve $\widehat{\mu}(c_d) = \mu_\infty$ for c_d and then solve (6.42) for c_a. The thickness of the slab is then given by (6.40).

7 Specific constitutive relationships.

7.1 Free energy.

In writing down the free energy, we adopt the classical Frenkel-Flory-Rehner approach where it is assumed that the elastic energy is carried solely by the polymer network, while the energy of mixing is carried by the solvent. The total free energy of the swollen polymeric gel can therefore be written as

$$\varphi(\mathbf{F}, c_R) = W(\mathbf{F}) + \varphi_m(c_R) + \mu_\infty c_R \tag{6.43}$$

As for the free energy of the polymer network (due to the elastic deformation of the network) we take the classical form constructed by Treloar [25]:

$$W(\mathbf{F}) = \frac{G}{2}\Big(|\mathbf{F}|^2 - 3 + \alpha \ln(\det \mathbf{F})\Big), \qquad G = \frac{kT}{\nu_p} \tag{6.44}$$

where G is the elastic shear modulus and ν_p represents the volume occupied by a single solid particle.

We take the chemical potential of the free unmixed solvent molecules in the surrounding region μ_∞. When the solvent diffuses into the polymer matrix, it changes its energy (per unit volume) by both change in relative volume and by mixing. Accordingly we take the Helmholtz free energy of the solvent molecules (within the gel) to be

$$\varphi_s(c_R) = \mu_\infty c_R + \varphi_m(c_R) \tag{6.45}$$

where the mixing energy φ_m is assumed to have the form proposed by Flory [12] and Huggins [18]:

$$\varphi_m(c_R) = kT\, c_R \left[\ln\left(\frac{\nu c_R}{1+\nu c_R}\right) + \frac{\chi}{1+\nu c_R}\right]. \tag{6.46}$$

where $\nu c_R = \phi_R$ is the volume occupied by the solvent per unit reference volume. Here k is Boltzmann's constant, T is temperature and χ is the Flory-Huggins interaction parameter.

8 Appendix-1

9 Preliminaries.

9.1 Terminology.

We are concerned with a body that grows by the sequential addition of layers of new material at a fixed surface Σ_a as shown schematically in Figure 1. Each new layer pushes away the previously formed layers and this typically leads to the generation of a stress field within the body.

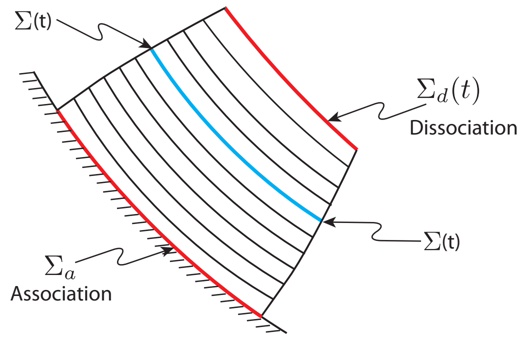

Figure 1: Schematic representation of the region $\mathcal{R}_t$ occupied by the body in physical space at the current instant t. The body grows by the sequential addition of layers of new material at the fixed "association surface" Σ_a, and the removal of material at the "dissociation surface" $\Sigma_d(t)$. All material points on the surface $\Sigma(t)$ were added to the body at the same previous instant.

We imagine the body of interest to involve a polymer network surrounded and infused by a solvent of monomers. A monomer can attach to a polymer chain at one end, and detach from it at the other end. The polymer and monomer are composed of the same basic chemical species. In our model, the problem involves a *single* molecular species that can exist in one of three "phases": it is a *free molecule* when it is contained in the fluid surrounding the body; a *solvent molecule* when it has infiltrated into a space within the polymer network; and a *polymer molecule* when it is attached to a polymer chain. We shall consistently use this terminology to distinguish between the three phases.

Solvent molecues are transformed into polymer molecules at the (fixed) *association surface* Σ_a. Polymer molecules are transformed back into free molecules at the *dissociation surface* $\Sigma_d(t)$. When we do not need to distinguish between these surfaces we shall simply refer to either or both as the *growth surface*. The portion of the boundary $\partial\mathcal{R}_t$ that is neither Σ_a nor $\Sigma_d(t)$ is denoted by $\Sigma(t)$; see Figure 1.

According to the picture we have in mind, the history of a typical molecule is as follows: it starts out as a free molecule outside the body and enters into the polymer network at the surface $\Sigma_d(t) \cup \Sigma(t)$. When this happens it becomes a solvent molecule. This molecule then diffuses through the body towards the association surface Σ_a. When it reaches Σ_a it transforms into a polymer molecule and is attached to one end of a polymer chain. The body then grows by the addition of a new layer of material at Σ_a. As each new layer forms, the previously formed layers are pushed outwards. At the dissociation surface $\Sigma_d(t)$ it maybe more favorable for a polymer molecule to detach from the body and transform back into a free molecule. The body grows if the rate of association exceeds the rate of dissociation; it shrinks in the opposite case; and when they balance, a circumstance referred to as treadmilling, the region $\mathcal{R}_t$ occupied by the body does not evolve, even though molecules continue to undergo the aforementioned process.

9.2 Configurations and kinematics.

We are concerned with growth taking place on a rigid stationary surface Σ_a in physical space which we refer to as the "association surface". Suppose that this surface is characterized parametrically by a vector-valued function $\tilde{\mathbf{y}}$ of surface coordinates X, Y that take values in some domain Π of the parametric X, Y-plane. Each $\tilde{\mathbf{y}}(X, Y)$ is a point in physical space of the association surface Σ_a:

$$\mathbf{y} = \tilde{\mathbf{y}}(X, Y), \qquad (X, Y) \in \Pi, \ \mathbf{y} \in \Sigma_a. \tag{6.47}$$

Since layers of new material are sequentially added to the body at Σ_a as illustrated schematically in Figure 1, we take the material manifold $\mathcal{R}_{\rm R}(t)$ to be the cartesian product of a surface Γ_a with a time-dependent interval $(Z_a(t), Z_d(t))$:

$$\mathcal{R}_R(t) = \Gamma_a \times (Z_a(t), Z_d(t)) \ \subset \mathbb{R}^4. \tag{6.48}$$

NNN explain NNN If the new layer of material is unstretched, then $\Gamma_a = \Sigma_a$. We shall allow for the possibility that when a new layer of material is formed it is subjected to a uniform in-plane equibiaxial stretching tangent to Σ_a. Each point $\mathbf{x} \in \mathcal{R}_R(t)$ can now be represented by

$$\mathbf{x} = \overline{\mathbf{x}}(X, Y, Z) \in \mathcal{R}_R(t) \qquad \text{for} \quad (X, Y) \in \Pi, \quad Z \in [Z_a(t), Z_d(t)]. \tag{6.49}$$

Observe that the material manifold $\mathcal{R}_{\rm R}(t)$ is a cylindrical hypersurface parallel to the Z-axis, each cross section of which is a copy of the surface Γ_a.

The coordinates (X, Y, Z) of a point $\mathbf{x}$ of the material manifold can be interpreted as follows:

(a) (X, Y) specifies where on Σ_a the particle was added to the body, and

(b) the section $Z = \mathsf{constant}$ of the cylinder comprises all material points added to the body at the same instant, say $t_0(Z)$.

Thus the body has been built-up by the sequential addition of layers, the most recent corresponding to $Z = Z_a(t)$. When a new layer is formed, it pushes the previously formed layers away from the association surface. Since each section $Z = \mathsf{constant}$ originated from Γ_a, the same surface coordinates (X, Y) can be used to identify points on it. At each instant t, the coordinates (X, Y, Z) uniquely label all points of the body and therefore $\mathcal{R}_{\rm R}(t)$ can serve as a *reference configuration.* The physical and reference spaces are illustrated schematically for a two-dimensional annular body in Figure 2.

Since all material points on the section $Z = \mathsf{constant}$ were added to the body at the same instant $t_0(Z)$, it follows that at some generic time t, the body consists of all layers formed during the time interval $(t_0(Z_d(t)), t_0(Z_a(t))$ with $t_0(Z_a(t)) = t$. If new material is being added to the body at Σ_a, the corresponding boundary $\Gamma_a(t)$ of $\mathcal{R}_{\rm R}(t)$ must translate parallel to the Z-axis in the negative direction, $\dot{Z}_a < 0$, thereby growing the interval $[Z_a(t), Z_d(t)]$ and thus incorporating new material points into $\mathcal{R}_{\rm R}(t)$. Conversely if material is being removed from Σ_a, $\Gamma_a(t)$ must translate in the positive Z-direction, $\dot{Z}_a > 0$, thereby shrinking the interval $[Z_a(t), Z_d(t)]$ corresponding to the removal material. An analogous situation takes place at the other boundary $\Gamma_d(t)$. This is illustrated schematically in Figure 2.

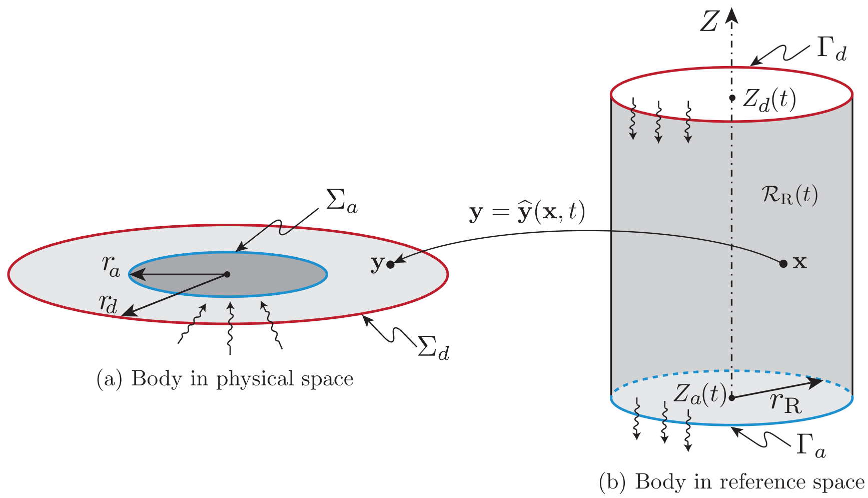

Figure 2: NNN need to fix. Stretched association NNN Schematic depiction of a body in two-dimensional physical space (left) where material is being added at the fixed surface Σ_a and lost at $\Sigma_d(t)$. The body grows by the *sequential* addition of rings (layers) of material at the fixed surface Σ_a, each new ring having radius r_a. We assume that each ring of new material is stretched circumferentially by λ_0, so that the corresponding unstressed reference region can be taken to be a ring Γ_a of radius r_R where $r_a = \lambda_0 r_R$. Therefore the corresponding region in reference space can be taken to be, so to speak, a stacking together of a one-parameter family of such rings: specifically, $\mathcal{R}_{\mathrm{R}}(t) = \Gamma_a \times (Z_a(t), Z_d(t))$ as shown on the right. Each cross section of the cylinder $\mathcal{R}_{\mathrm{R}}(t)$ is a copy of Γ_a. The two ends $\Gamma_a(t)$ and $\Gamma_d(t)$ of the cylinder correspond to Σ_a and $\Sigma_d(t)$, and they can move in the vertical direction thus adding or removing material points from $\mathcal{R}_{\mathrm{R}}(t)$ as suggested by the squiggly arrows.

The material manifold is placed in physical space by the mapping $\mathbf{y}(\cdot, t)$ that takes each material point $\mathbf{x} \in \mathcal{R}_R(t)$ into a point $\mathbf{y}(\mathbf{x}, t) \in \mathcal{R}_t$ of physical space where $\mathcal{R}_t$ is the region occupied by the body at time t:

$$\mathbf{y} = \mathbf{y}(\mathbf{x}, t), \qquad \mathbf{x} \in \mathcal{R}_R(t), \ \mathbf{y} \in \mathcal{R}_t. \tag{6.50}$$

Observe from (6.49) and (6.50) that

$$\mathbf{y} = \overline{\mathbf{y}}(X, Y, Z, t) = \mathbf{y}(\overline{\mathbf{x}}(X, Y, Z), t). \tag{6.51}$$

Figure 3 schematically illustrates the body comprised of a sequence of layers $Z = \mathsf{constant}$. The particle velocity and deformation gradient tensor are defined in the usual way by

$$\mathbf{v} = \frac{\partial \mathbf{y}}{\partial t}, \qquad \mathbf{F} = \frac{\partial \mathbf{y}}{\partial \mathbf{x}}. \tag{6.52}$$

In the presence of surface growth it is important to distinguish between a point on the growth surface and the material point that happens to be at that same location at that instant. Consider a point $\mathbf{x}_b(t)$ on the *association surface* $Z = Z_a(t)$ in the reference configuration. Its velocity $\mathbf{V}_R = d\mathbf{x}_b/dt$ is found by differentiating $\mathbf{x}_b(t) = \overline{\mathbf{x}}(X, Y, Z_a(t))$ with respect to t at fixed X, Y:

$$\mathbf{V}_R = \frac{d}{dt}\overline{\mathbf{x}}(X, Y, Z_a(t)) = \dot{Z}_a(t)\frac{\partial \overline{\mathbf{x}}}{\partial Z} = \dot{Z}_a(t)\mathbf{e}_Z = -\dot{Z}_a(t)\mathbf{n}_R = V_R \mathbf{n}_R \qquad \text{on } \Gamma_a, \tag{6.53}$$

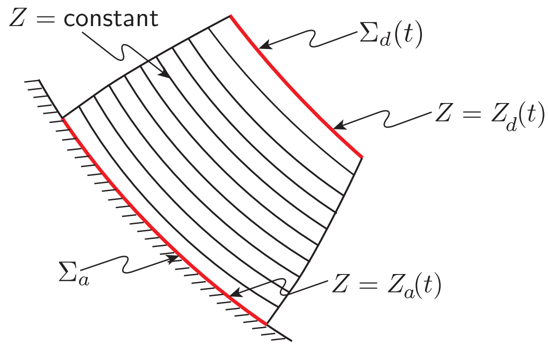

Figure 3: Schematic representation of the region $\mathcal{R}_t$ occupied by the body at the current instant. Each section $Z = \mathsf{constant}$ is comprised of particles added to the body at the same time $t_0(Z)$. The particles on $Z = Z_a$ were added at the current instant t; those on $Z = Z_d$ were added at a previous instant t_1.

where

$$V_R = -\dot{Z}_a(t) \qquad \text{on } \Gamma_a. \tag{6.54}$$

If there is no growth, the referential region $\mathcal{R}_R$, and $Z_a(t)$, do not depend on time whence $\mathbf{V}_R$ vanishes.

Corresponding formulae hold at the *dissociation surface* $Z = Z_d(t)$. In particular, the analog of (6.53) is

$$\mathbf{V}_R = \frac{d}{dt}\overline{\mathbf{x}}(X, Y, Z_d(t)) = \dot{Z}_d(t)\frac{\partial \overline{\mathbf{x}}}{\partial Z} = \dot{Z}_d(t)\mathbf{e}_Z = \dot{Z}_d(t)\mathbf{n}_R = V_R\mathbf{n}_R \qquad \text{on } \Gamma_d, \tag{6.55}$$

where

$$V_R = \dot{Z}_d(t) \qquad \text{on } \Gamma_d. \tag{6.56}$$

In the current configuration (for both Σ_a and $\Sigma_d(t)$), a point on the boundary of the body is $\mathbf{y}_b(t) = \mathbf{y}(\mathbf{x}_b(t), t) = \mathbf{y}(\overline{\mathbf{x}}(X, Y, Z_a(t)), t)$. Differentiating this with respect to t at fixed X, Y gives the velocity $\mathbf{V} = d\mathbf{y}_b/dt$ of this point:

$$\mathbf{V} = \frac{d}{dt}\mathbf{y}(\overline{\mathbf{x}}(X, Y, Z_a(t)), t) = \mathbf{F}\mathbf{V}_R + \mathbf{v}, \tag{6.57}$$

where $\mathbf{v}$ is particle velocity. In general, the velocity $\mathbf{V}$ of a point on the boundary in the current configuration differs from the velocity $\mathbf{v}$ of the material point that happens to be at that same location at that time. If there is no growth then $\mathbf{V}_R = \mathbf{0}$ in which event $\mathbf{V} = \mathbf{v}$.

Observe that the association surface Σ_a is characterized through (6.47) as $\mathbf{y} = \tilde{\mathbf{y}}(X, Y)$ whereas (6.51) provides the alternate (equivalent) characterization $\mathbf{y} = \mathbf{y}(\overline{\mathbf{x}}(X, Y, Z_a(t)), t)$. Equating these two representations and differentiating with respect to t at fixed X, Y gives $\mathbf{F}\mathbf{V}_R + \mathbf{v} = \mathbf{0}$ on Σ_a whence the propagation velocity of the association surface in physical space vanishes:

$$\mathbf{V} = \mathbf{0} \qquad \text{on } \Sigma_a. \tag{6.58}$$

This, of course, is consistent with our formulation (see remark preceding (6.47)) where we assumed the association surface to be stationary. From (6.53), (6.57) and (6.58) we find that the particle velocity on the association surface is

$$\mathbf{v} = -V_R\,\mathbf{F}\mathbf{n}_R, \quad V_R = -\dot{Z}_a(t) \qquad \text{on } \Sigma_a. \tag{6.59}$$

Let $\mathbf{n}$ and $\mathbf{n}_R$ denote the respective unit outward normal vectors at corresponding points on the boundaries $\partial\mathcal{R}_t$ and $\partial\mathcal{R}_R$ in the current and reference configurations, and let dA_y and dA_x be corresponding differential area elements. We know these are related by $\mathbf{n}\,dA_y = J\mathbf{F}^{-T}\mathbf{n}_R\,dA_x$; e.g. see Chadwick [6]. Then using this and (6.57) shows that

$$(\mathbf{V} - \mathbf{v}^-)\cdot\mathbf{n}\,dA_y = J^-\,\mathbf{V}_R\cdot\mathbf{n}_R\,dA_x. \tag{6.60}$$

Suppose that $(\mathbf{V} - \mathbf{v})\cdot\mathbf{n} > 0$ at some point on the boundary of the body at some instant. Then this boundary point is instantaneously moving faster than the material point located at that same position. Thus a volume $(\mathbf{V} - \mathbf{v})\cdot\mathbf{n}\ dA_y$ "opens up" and is filled by new molecules that are added to the body. By (6.60), this corresponds to $\mathbf{V}_R\cdot\mathbf{n}_R > 0$. Conversely if $(\mathbf{V} - \mathbf{v})\cdot\mathbf{n} < 0$, or equivalently $\mathbf{V}_R\cdot\mathbf{n}_R < 0$, the boundary is moving more slowly than the material point and so a volume $(\mathbf{v} - \mathbf{V})\cdot\mathbf{n}\,dA_y$ is "lost" due to the detachment of molecules. Thus *association corresponds to* $\mathbf{V}_R\cdot\mathbf{n}_R > 0$ *and dissociation corresponds to* $\mathbf{V}_R\cdot\mathbf{n}_R < 0$:

$$\text{Association}: V_R > 0, \qquad \text{Dissociation}: V_R < 0, \tag{6.61}$$

where $\mathbf{V}_R = V_R\mathbf{n}_R$

If ρ_R is the referential mass density of the material, then the mass rate at which material is being added to the body at a differential element dA_x of $\Gamma_i, i = a, d$ is

$$\rho_R\,V_R\,dA_x.$$

It follows from (6.60) that

$$\rho_{R1}\,V_R\,dA_x = \rho_1\,(\mathbf{V} - \mathbf{v})\cdot\mathbf{n}\,dA_y,$$

where $\rho = \rho_R/J$ is the mass density per unit current volume.

Skalak et al. provide a careful discussion of the kinematics of surface growth in [21]. In particular they refer to the velocity with which "material points move away from the surface of growth",

$$\mathbf{V}_G = \mathbf{v} - \mathbf{V}, \tag{6.62}$$

as the *growth velocity.* Note from (6.57) and (6.62) that

$$\mathbf{V}_G = -\mathbf{F}\mathbf{V}_R, \tag{6.63}$$

whence $\mathbf{V}_G = \mathbf{0}$ if and only if $\mathbf{V}_R = \mathbf{0}$. Skalak et al. [22] point out that the growth velocity $\mathbf{V}_G$ need not be perpendicular to the growth surface, and study the geometry of various structures that arise from different choices of the direction of $\mathbf{V}_G$.

Turning to the association surface Σ_a, we have the boundary condition

$$\mathbf{V} = \mathbf{0} \qquad \text{on } \Sigma_a. \tag{6.64}$$

Our immediate goal is to write this boundary condition in a more convenient form. the reason association takes place at Σ_a is because this surface has been treated with a certain chemical that attracts the free molecules. This chemical treatment creates a distribution of binding sites on Σ_a to which the growing polymer chains attach. These sites are assumed to occur at fixed locations on Σ_a and so the tangential deformation of the gel, parallel to the support surface, is predetermined. Suppose that this corresponds to a prescribed two-dimensional isotropic stretch λ_0 parallel to Σ_a. Based on this we require that, at each point on the association surface, $\mathbf{F}\boldsymbol{\ell} = \lambda_0\boldsymbol{\ell}$ for all unit vectors $\boldsymbol{\ell}$ perpendicular to $\mathbf{n}_R$. This implies that $\mathbf{F}$ can be expressed as

$$\mathbf{F} = \lambda_0\mathbf{I} + \mathbf{a}\otimes\mathbf{n}_R \qquad \text{on } \Gamma_a, \tag{6.65}$$

for some arbitrary (possibly $\mathbf{x}$ and t-dependent) vector $\mathbf{a}$. For this $\mathbf{F}$,

$$J = \det\mathbf{F} = \lambda_0^2(\lambda_0 + \mathbf{a}\cdot\mathbf{n}_R), \qquad \mathbf{F}^{-1} = \lambda_0^{-1}\left[\mathbf{I} - \frac{\lambda_0^2}{J}\,\mathbf{a}\otimes\mathbf{n}_R\right] \qquad \text{on } \Gamma_a. \tag{6.66}$$

On using this in the relation $\mathbf{n}\; dA_y = J\mathbf{F}^{-T}\mathbf{n}_R\; dA_x$ between area elements on a surface in the current and reference configurations, e.g. see Chadwick [6], one finds (as one would expect) that

$$dA_y = \lambda_0^2\; dA_x, \qquad \mathbf{n} = \mathbf{n}_R \qquad \text{on } \Gamma_a. \tag{6.67}$$

Recall from (6.59) that the particle velocity at the association surface Σ_a is $\mathbf{v} = -V_R\mathbf{F}\mathbf{n}_R$. This can be simplified using (6.65) and $(6.67)_2$ to read

$$\mathbf{v} = -\lambda_0 V_R\mathbf{n} - V_R\mathbf{a} \qquad \text{on } \Sigma_a. \tag{6.68}$$

We now assume that the growth velocity $\mathbf{V}_G$ is normal to the association surface. Note however by (6.62) and (6.64) that the growth velocity equals the particle velocity at Σ_a. Consequently the particle velocity $\mathbf{v}$ must also be normal to Σ_a and therefore $\mathbf{a}$ must be parallel to $\mathbf{n}$. So we may write

$$\mathbf{a} = (\lambda - \lambda_0)\mathbf{n},$$

for some scalar λ whence

$$\mathbf{F} = \lambda\,\mathbf{n}\otimes\mathbf{n} + \lambda_0(\mathbf{I} - \mathbf{n}\otimes\mathbf{n}), \qquad J = \lambda\lambda_0^2 \qquad \text{on } \Gamma_a. \tag{6.69}$$

Thus λ represents the stretch normal to Σ_a (while λ_0 is the tangential stretch). The particle velocity at the association surface given by (6.68) now reduces to

$$\mathbf{v} = \lambda\dot{Z}_a\,\mathbf{n} \qquad \text{on } \Sigma_a, \tag{6.70}$$

having used $V_R = -\dot{Z}_a$. We require the boundary condition (6.70) to hold on the association surface. Observe that if there is no growth, $\dot{Z}_a = 0$, then $\mathbf{v} = \mathbf{0}$.

Association surface Σ_a: We now turn to the dissipation rate at Σ_a. Recall that $\mathbf{V} = \mathbf{0}$. The inflow of free energy per unit area per unit time *into* Σ_a carried by the incoming species-2 particles is $\rho_2^- \psi_2^- \mathbf{v}_2^- \cdot \mathbf{n}$. The outflow of free energy per unit area per unit time from Σ_a carried by the outgoing species-1 particles is $\rho_1^- \psi_1^- (-\mathbf{v}_1^- \cdot \mathbf{n})$ plus $\psi_a (-\mathbf{v}_1^- \cdot \mathbf{n})$. Here we are assuming that a certain amount of energy (per unit area) ψ_a is added to the particles by the chemical agent promoting association. Thus the increase in energy at Σ_d is

$$= \rho_1^- \psi_1^- (-\mathbf{v}_1^- \cdot \mathbf{n}) + \psi_a(-\mathbf{v}_1^- \cdot \mathbf{n}) - \rho_2^- \psi_2^- \mathbf{v}_2^- \cdot \mathbf{n} = (\rho^- \psi^- + \psi_a)\,(-\mathbf{v}_1^- \cdot \mathbf{n}) - \psi_2^- \,\mathbf{j}^- \cdot \mathbf{n}, \qquad (6.71)$$

where we have used $\rho\psi = \rho_1\psi_1 + \rho_2\psi_2$ and $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$ in getting this. The rate of working (per unit area) by the traction on Σ_a is

$$\mathbf{T}_1^-(-\mathbf{n}) \cdot \mathbf{v}_1^- + \mathbf{T}_2^-(-\mathbf{n}) \cdot \mathbf{v}_2^-,$$

which can be written equivalently as

$$-\,\mathbf{T}^-\mathbf{n} \cdot \mathbf{v}_1^- - (\psi_2^- - \mu)\,\mathbf{j}^- \cdot \mathbf{n}, \qquad (6.72)$$

having used $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2, \mathbf{T}_2 = \rho_2(\psi_2 - \mu)\mathbf{I}$ and $\mathbf{j} = \rho_2(\mathbf{v}_2 - \mathbf{v}_1)$.

Remark: Look if how I added the energy source ψ_a is sensible.

Therefore the *dissipation rate* at the surface Σ_a is found by subtracting (6.71) from (6.72) to be

$$\dot{\mathbb{D}}_a = \int_{\mathcal{S}_a} \Big[(\rho^-\psi^- + \psi_a)\mathbf{v}_1^- \cdot \mathbf{n} + \mu\mathbf{j}^- \cdot \mathbf{n} - \mathbf{T}^-\mathbf{n} \cdot \mathbf{v}_1^-\Big]\, dA_y. \qquad (6.73)$$

The flux $\mathbf{j}^-$ can be eliminated by using the mass balance jump condition (4.3) which leads to

$$\dot{\mathbb{D}}_a = \int_{\mathcal{S}_a} \Big[-\mathbf{T}^- + \big[\rho^-(\psi^- - \mu) + \psi_a\big]\mathbf{I}\Big]\mathbf{v}_1^- \cdot \mathbf{n}\, dA_y. \qquad (6.74)$$

Finally on using $\mathbf{v}_1^- - \mathbf{V} = -\mathbf{F}_1^- \mathbf{V}_R$, $\mathbf{V} = \mathbf{0}$ and (3.1) we have the referential form

$$\dot{\mathbb{D}}_a = \int_{\mathcal{S}_{Ra}} \Big[\mathbf{S}^-\mathbf{n}_R \cdot \mathbf{F}_1^-\mathbf{n}_R - \rho^- J_1^-(\psi^- - \mu) - \psi_a J_1^-\Big]\; V_R\, dA_x. \qquad (6.75)$$

where

$$\mathbf{S}^- = J_1^- \mathbf{T}^- \mathbf{F}_1^{-\,-T}. \qquad (6.76)$$

The *driving force on the association surface* is therefore

$$\boxed{f_a = \mathbf{S}^-\mathbf{n}_R \cdot \mathbf{F}_1^-\mathbf{n}_R - (\varphi^- - \rho^- J_1^- \mu) - \psi_a J_1^- \qquad \text{on } \Gamma_a,} \qquad (6.77)$$

having used $\varphi = \rho\psi J_1$ and the dissipation inequality requires

$$f_a V_R \geq 0 \qquad \text{on } \Gamma_a.$$

10 Appendix-2

10.1 The latent energy

We now consider the latent energy $\Delta\varphi$ associated with transduction. The respective processes underlying association and dissociation are different and so we must consider them separately. For clarity let us refer to a molecule as a "free molecule" when it is in the solution surrounding the body, a "solvent molecule" when it is embedded in the gel, and as a "polymer molecule" when when it is attached to a polymer chain in the gel. Moreover, suppose that the Helmholtz free energy per unit reference volume is the sum of two terms, φ_p and φ_s, associated with the polymer matrix and solvent respectively:

$$\varphi(\mathbf{F}, c_R) = \varphi_p(\mathbf{F}, c_R) + \varphi_s(\mathbf{F}, c_R), \tag{6.78}$$

each representing energy per unit reference volume. The term φ_s can be further split into a term φ_0 associated free molecules and a term φ_m due to mixing which we shall do in Section 11.

The latent energy of association. As mentioned previously, the surface at which association occurs is taken to be rigid, impermeable and stationary. Then the process of association involves a solvent molecule reaching this surface from the interior of the gel and being transformed into a polymer molecule. The corresponding energy therefore changes from φ_s to φ_p and so

$$\Delta\varphi = \varphi_s - \varphi_p, \qquad \text{(association surface)}. \tag{6.79}$$

Observe from (**??**) that, in the absence of stress, the driving force is $f = \Delta\varphi = \varphi_s - \varphi_p$. Recalling that $V_R > 0$ at the association surface, and therefore from the dissipation inequality that $f \geq 0$, we conclude that $\varphi_p \leq \varphi_s$ is necessary for association.

The latent energy of dissociation. The process of dissociation involves a polymer molecule reaching this surface from the interior of the body, transforming into a free molecule that is released into the surrounding solvent. The associated energy therefore changes from φ_p to φ_0 and so

$$\Delta\varphi = \varphi_0 - \varphi_p, \qquad \text{(dissociation surface)}. \tag{6.80}$$

Here the driving force in the absence of stress is $f = \Delta\varphi = \varphi_0 - \varphi_p$ which must be ≤ 0 since $V_R < 0$ at the disssociation surface. Thus $\varphi_p \geq \varphi_0$ is necessary for dissociation.

10.2 Kinetics of association and dissociation.

Let t

$$\dot{G} = k^+_{\text{on}}\, c - k^+_{\text{off}} =$$

$$\dot{G} = k^+_{\text{on}}\, c_R$$

$$k^+_{\text{on}} = A \text{ Exp}\left(-\frac{\Delta G}{kT}\right)$$

Energetics and driving force for association: Consider a solvent molecule that is part of the gel, which arrives at the association surface Σ_a. Here it is attached to the tip of a polymer filament and becomes part of the polymer. Note that it is part of the gel, both before and after association, the transformation being from one type of constitutent to another. Let μ_1 and μ_2 be the chemical potential energies of the molecule in these two respective states. Turning next to the Helmholtz free energy $\psi(\mathbf{F}, c_R)$, take it to comprise of two parts, the elastic energy of the polymer network $\psi_e(\mathbf{F})$ and the ("mixing") energy of the solvent molecules $\psi_m(\mathbf{F}, c_R)$ in the gel, both per unit reference volume:

$$\psi(\mathbf{F}, c_R) = (1 - \nu c_R)\psi_e(\mathbf{F}) + \nu c_R \psi_m(\mathbf{F}, c_R). \tag{6.81}$$

The molecule under discussion thus has energy $\psi_m(\mathbf{F}, c_R)/c_R$ before transformation and energy $\psi_e(\mathbf{F})/c_R$ after transformation. Thus collecting all of the preceding terms, the change in energy of the molecule is

$$\Delta\psi \;=\; \Big(\mu_1 c_R + \psi_m(\mathbf{F}, c_R)\Big) \;-\; \Big(\mu_2 c_R + \psi_e(\mathbf{F})\Big). \tag{6.82}$$

In the course of undergoing this transformation it has move the previously formed layer of material away and must expend power of $\mathbf{S}\mathbf{N}_R \cdot \mathbf{F}\mathbf{n}_R$ in order to do this. Thus the driving force during this transformation process is

$$f = \mathbf{S}\mathbf{N}_R \cdot \mathbf{F}\mathbf{n}_R + \Delta\psi = \tag{6.83}$$

The number of solvent molecules arriving on some differential area dA_x of the association surface per unit time is $V_R\, dA_X = \mathbf{V}_R \cdot \mathbf{n}_R\, dA_x$ times the number of solvent molecules per unit reference volume, i.e. c_R. The Helmholtz free energy $\psi(\mathbf{F}, c_R)$ characterizes the total free energy of the gel per unit reference volume. It is composed of two parts, the elastic energy of the polymer molecules $\psi_e(\mathbf{F}, c_R)$ and the ("mixing") energy of the solvent molecules $\psi_m(\mathbf{F}, c_R)$, both per unit reference volume. Thus the inflow of energy into the area dA_x of the association surface per unit time is

$$(c_R\mu_\infty + \psi_m)V_R dA_x.$$

The outflow of energy away from the area dA_x of the association surface per unit time is

$$(c_R\mu_{0R} + \psi_e)V_R dA_x.$$

Therefore for the latent energy $\Delta\psi$ at the association surface we have

$$\Delta\psi = (c_R\mu_{0R} + \psi_e) - (c_R\mu_\infty + \psi_m)$$

Next consider the dissociation surface. Here solvent molecules that comprise the polymeric part of the gel arrive at this surface and are transformed into free solvent molecules (that are part of the solution). Let μ_1 and μ_{R1} be the chemical potential energies of a solvent molecule in these two respective states. The part of the Helmholtz free energy that characterizes the elastic energy of the polymer molecules is $\psi_e(\mathbf{F}, c_R)$ and we ignore any elastic energy of the solvent. Thus the inflow of energy into an area dA_x of the dissociation surface per unit time is

$$(c_R\mu_1 + \psi_e)V_R dA_x.$$

The outflow of energy away from the area dA_x of the dissociation surface per unit time is

$$(c_R\mu_{R1})V_R dA_x.$$

Therefore for the latent energy $\Delta\psi$ at the dissociation surface we have

$$\Delta\psi = (c_R\mu_{R1}) - (c_R\mu_1 + \psi_e).$$

The rate of working needed to move the particles outwards is $(\mathbf{Sn}_R \cdot \mathbf{Fn}_R)dA_x\, V_R$ and so the dissipaton rate per unit area at this surface is

$$\mathsf{D}_{association} = (c_R\mu_\infty + \psi_m)V_R - (c_R\mu_{0R} + \psi_e)V_R dA_x - (\mathbf{Sn}_R \cdot \mathbf{Fn}_R)V_R \stackrel{\text{def}}{=} fV_R \geq 0,$$

where the driving force f is given by

$$f = (c_R\mu_\infty + \psi_m) - (c_R\mu_{0R} + \psi_e) - (\mathbf{Sn}_R \cdot \mathbf{Fn}_R)$$

We now turn to the kinetics of association/dissociation. A specific forms for these kinetic relations will be given in Section 11. Here we make some general remarks on the form of such an equation. As discussed previously, the referential speed V_R is a measure of the rate at which molecules are added to or removed from the polymer at some location on the boundary, with $V_R > 0$ corresponding to association and $V_R < 0$ to dissociation.

11 Specific constitutive equations.

Before solving the preceding initial-bondary value problem we must choose a specific set of constitutive relations.

11.1 Free energy.

We take the Helmholtz free energy per reference volume of the free unmixed molecules in the surrounding region, to be

$$\varphi_0 = \mu_\infty c_0 \tag{6.84}$$

where the constant μ_∞ is the chemical potential in this region and c_0 is the concentration of free molecules.

When the solvent diffuses into the polymer matrix, it changes its energy (per unit volume) by both change in relative volume and by mixing. Accordingly we take the Helmholtz free energy of the solvent molecules (within the gel) to be composed of two parts

$$\varphi_s(c_R) = \nu c_R \varphi_0 + \varphi_m(c_R) \tag{6.85}$$

where νc_R is the fraction of volume occupied by the solvent per unit reference volume and φ_m is the mixing energy. Since in the solvent region $\nu_s c_R = \nu_s c = 1$ this is consistent with the definition in (6.84). NNN I don't understand NNN

The free energy of mixing is assumed to have the form proposed by Flory [12] and Huggins [18]:

$$\varphi_m(c_R) = kT\, c_R\; \left[\ln\left(\frac{\nu_s c_R}{1+\nu_s c_R}\right) + \frac{\chi}{1+\nu_s c_R}\right]. \tag{6.86}$$

Here k is Boltzmann's constant, T is temperature and χ is the Flory-Huggins interaction parameter.

As for the free energy of the polymer network (due to the elastic deformation of the network) we take the classical form constructed by Treloar [25] with some allowance for compressibility:

$$\varphi_p(\mathbf{F}) = \frac{G}{2}\Big(|\mathbf{F}|^2 - 3 + \alpha\ln(\det\mathbf{F})\Big), \qquad G = \frac{kT}{\nu_p} \tag{6.87}$$

where G is the elastic shear modulus and ν_p represents the volume occupied by a single solid particle. For further use we define the volume ratio

$$\upsilon = \frac{\nu_s}{\nu_p} \tag{6.88}$$

between a particle in the solvent and a particle in the polymer. (Note that $N = 1/\nu_p$ is the number of cross-linked units per unit reference volume).

The total free energy of the swollen polymeric gel can therefore be written as

$$\varphi(\mathbf{F}, c_R) = \nu_s c_R \varphi_0 + \varphi_m(c_R) + \varphi_e(\mathbf{F}) \tag{6.89}$$

In the preceding formulation we have adopted the classical Frenkel-Flory-Rehner approach were it is assumed that the elastic energy is carried solely by the polymer network, while the energy of mixing is carried by the solvent.

11.2 Kinetics of solvent flux.

As mentioned previously in the one-dimensional context (see (6.20)) for the kinetic law for species diffusion we take the classical model (Feynmann, Leighton and Sands, [9])

$$\mathbf{j} = -mc\,\mathrm{grad}\,\mu, \qquad m = \frac{D}{kT} > 0, \tag{6.90}$$

where the diffusion coefficient D is a material constant.

11.3 Kinetics of association and dissociation.

At the microscopic level growth is driven by a *Brownian Ratchet* mechanism of polymerization/depolymerization, a process governed by random walks and thermal fluctuations (refs to Oster Mogliner x2 ???). A broad illuminating review of theories related to the transduction of chemical energy into mechanical energy by polymerization can be found in (Theriot ???).

In the present study we are concerned with modeling the phenomenon of surface growth from a macroscopic point of view using the tools of continuum mechanics. We consider a simplified framework in which chemical reactions take place only at the free ends of the polymer chains, and these ends are assumed to exist only at the boundaries of the body. These chains have an intrinsic polarity and therefore the reaction rates are different at the two ends where monomers may both attach and detach with different probabilities. The net rate of growth k is typically related to the difference between the rate of attachment (association) $k_{\rm on}$ and the rate of detachment (dissociation) $k_{\rm off}$. At the association surface we have $k > 0$ while at the dissociation surface $k < 0$.

Recall that the net reaction rate k in our model is the velocity V_R of the growth surface in the reference frame: $k = V_R$. We take the reaction rates to be functions of the driving force f. Being a local quantity in a continuum framework, the present definition of the driving force f does not distinguish between the two competing mechanisms of association and dissociation but is concerned with the power input invested in advancing the interface at a given rate. We assume that the minimum energy that must be available to induce the chemical reaction is the work invested by the driving force in binding/unbinding a single monomer, i.e. νf. We assume further that the process is thermally activated so that the kinetics has the Arrhenius form

$$V_R = V(f) = \begin{cases} b_a \left(e^{\frac{\nu f}{kT}} - \mathrm{e}^{-\frac{\nu f}{kT}} \right) = 2b_a \sinh\left(\dfrac{\nu f}{kT}\right), & f \geq 0, \text{ (association)}, \\ b_d \left(e^{\frac{\nu f}{kT}} - \mathrm{e}^{-\frac{\nu f}{kT}} \right) = 2b_d \sinh\left(\dfrac{\nu f}{kT}\right), & f \leq 0, \text{ (dissociation)}, \end{cases} \tag{6.91}$$

with (positive) reaction constants b_a and b_d. In the limit of small departures from thermodynamic equilibrium (**??**) reduces to the linear form

$$V_R = V(f) = \begin{cases} \dfrac{2\nu b_a}{kT} f, & f \geq 0, \text{ (association)}, \\ \dfrac{2\nu b_d}{kT} f, & f \leq 0, \text{ (dissociation)}. \end{cases} \tag{6.92}$$

It should be noted that though it is tempting to propose that the first exponential term in (**??**) corresponds to $[c]k_{on}$ while the second term to k_{off}, this is immediately found to be inconsistent since the first term does not necessarily vanish with $c = 0$.

11.4 The latent energy

We now consider separately the latent energy of association and dissociation. It should be emphasized that this process is not symmetric in the sense that association does not involve the same absolute level of latent energy as does dissociation. This is due to the different mechanisms involved in these transitions and the different loading conditions at which they occur. Indeed, macroscopic growth is dependent on the competition between association and dissociation.

A necessary condition for initiation of growth, when both surfaces theoretically unite, is that association is favorable, namely that $V_a + V_d > 0$. Notice that, by definition, V, f are positive if they point in the outward normal direction to the interface in the reference setting. Hence, association implies $V_a, f_a > 0$ and dissociation implies $V_d, f_d < 0$. Nevertheless, under certain conditions the driving force may change signs, implying that a growth surface may begin to dissociate and vice versa, as reflected by (**??**).

The latent energy of association. Considering an impermeable growth surface and without any external mechanisms of energy input there is no transport of potential energy into the body at the association surface and the chemical potential difference $\Delta\psi$ is solely due to a microscopic mechanism of binding solvent particles to the solid. In other words, the Brownian ratchet mechanism imposes a jump in energy level from the free energy of a single monomer in the solvent state to the free energy of the same monomer if it were attached to the network - the latent energy. Hence, at the association surface, a unit of reference volume of solvent particles that has potential energy ψ_s can reduce its energy to ψ_p by attaching to the polymer network. Accordingly we can write the energy difference by

$$\Delta\psi_a = \psi_s - \psi_p > 0 \tag{6.93}$$

where the inequality $\psi_p < \psi_s$ is a necessary condition for polymerization. Note that this relation does not change if the growth surface is permeable (i.e. allows for external solvent to cross into the body) since that flux of solvent does not effect the configuration of the body and the growth reaction depends only on the conditions on the side of the surface where growth is permitted. Hence the effect of permeability comes in through the boundary conditions.

The latent energy of dissociation. At the depolymerization surface the dissociated particles do not necessarily return into the body and the latent energy is solely due to transport across the singularity surface. Therefore we write

$$\Delta\psi_d = [\![\psi]\!] \tag{6.94}$$

where the double square brackets denote the jump of the inserted quantity across the interface ($[\![\psi]\!] = \psi^+ - \psi^-$). Notice that the positive direction is along the outward facing normal in the reference configuration, and since material is being dissociated the interface moves in the opposite direction, towards the lower potential. Hence, given the definitions in (**??**) we further specify the above relation to the form

$$\Delta\psi_d = [\![\psi_s]\!] - \psi_p < 0 \tag{6.95}$$

NOTE (added Feb 2017) Let the effective volume of a particle in the polymer phase be ν_p, and let c_p be the polymer concentration in particles per unit current volume. Then the volume that the polymer particles take up in a unit volume is $\nu_p c_p = 1/J_1$. Likewise the volume occupied by solvent particles is $\nu_s c_s = 1/J_2$. Since these are the only particles in the system they are related by

$$\nu_s c_s + \nu_p c_p = 1. \tag{6.96}$$

The concentrations per unit reference volume are $c_p^R = J c_p$ and $c_s^R = J c_s$ and so

$$\nu_s c_s^R + \nu_p c_p^R = J. \tag{6.97}$$

Let $\dot{g}_R$ be the dissociation rate on $\partial\mathcal{R}_R$, specifically, the number of molecules transforming from the polymer phase to the free molecular phase (and thereby being inserted into the surrounding fluid) per unit reference area per unit time. Since these molecules are supplied by the polymer, $\dot{g}_R$ is the rate of loss of polymer molecules from the body, and since these molecules are added to the fluid it is also the rate of addition of molecules into the fluid. The rate of change of polymer molecules in $\mathcal{R}_R$ must obey

$$\frac{d}{dt}\int_{\mathcal{R}_R} c_p^R \, dV_x = -\int_{\partial\mathcal{R}_R} \dot{g}_R \, dA_x. \tag{6.98}$$

The rate of change of solvent molecules in $\mathcal{R}_R$ (NNN no $\mathbf{j}$ is not flux acros the non-material boundary NNN) must similarly obey

$$\frac{d}{dt}\int_{\mathcal{R}_R} c_s^R \, dV_x = \int_{\partial\mathcal{R}_R} -\mathbf{j}_R^+ \cdot \mathbf{n}_R \, dA_x + \int_{\partial\mathcal{R}_R} \dot{g}_R \, dA_x. \tag{6.99}$$

where the first integral on the right hand side represents the influx of solvent molecules into $\mathcal{R}_R$ from the surrounding fluid. (NNN Seems like this is assuming that all polymer molecules that get dissociated get added back into the body as solvent molecules and that none go into the surrounding liquid. Yes? Also (6.106) disagrees with (**??**). NNN) It is easy to simplify these to get the respective equations

$$\int_{\partial\mathcal{R}_R} \dot{g}_R \, dA_x = \int_{\partial\mathcal{R}_R} [\![c_p^R]\!] \, \mathbf{V}_R \cdot \mathbf{n}_R dA_x, \tag{6.100}$$

$$\int_{\partial\mathcal{R}_R} \dot{g}_R \, dA_x = -\int_{\partial\mathcal{R}_R} [\![c_s^R]\!] \mathbf{V}_R \cdot \mathbf{n}_R \, dA_x + \int_{\partial\mathcal{R}_R} [\![\mathbf{j}_R \cdot \mathbf{n}_R]\!] \, dA_x, \tag{6.101}$$

Thus we have the following two alternate equations involving the dissociation rate $\dot{g}_R$:

$$\int_{\partial\mathcal{R}_R} \dot{g}_R \, dA_x = \int_{\partial\mathcal{R}_R} [\![c_p^R]\!] \, \mathbf{V}_R \cdot \mathbf{n}_R dA_x = -\int_{\partial\mathcal{R}_R} [\![c_s^R]\!] \mathbf{V}_R \cdot \mathbf{n}_R \, dA_x + \int_{\partial\mathcal{R}_R} [\![\mathbf{j}_R \cdot \mathbf{n}_R]\!] \, dA_x \tag{6.102}$$

In the calculation above we considered the entire region $\mathcal{R}_R$ occupied by the body. We could instead have considered an arbitrary subregion $\mathcal{D}_R$ which has part of its boundary coinciding with $\partial\mathcal{R}_R$, the result of which can be localized to get

$$\dot{g}_R = [\![\mathfrak{c}_p^R]\!] \, \mathbf{V}_R \cdot \mathbf{n}_R = -[\![c_s^R]\!] \mathbf{V}_R \cdot \mathbf{n}_R \ + [\![\mathbf{j}_R \cdot \mathbf{n}_R]\!] \tag{6.103}$$

and so we have the following equation at the growth surface expressing the balance of molecules:

$$[\![\mathbf{j}_R \cdot \mathbf{n}_R]\!] = [\![c_s^R + c_p^R]\!]\mathbf{V}_R \cdot \mathbf{n}_R \,. \tag{6.104}$$

The Eulerian version of this is

$$[\![\mathbf{j} \cdot \mathbf{n}]\!] = [\![(c_s + c_p)(\mathbf{V} - \mathbf{v}) \cdot \mathbf{n}]\!] \,. \tag{6.105}$$

Remark: Observe that if $\nu_p = \nu_s \stackrel{\text{def}}{=} \nu$, equation (6.96) tells us that $c_s + c_p = 1/\nu$ and so (6.105) specializes to

$$[\![\mathbf{j} \cdot \mathbf{n}]\!] = \frac{1}{\nu}[\![(\mathbf{V} - \mathbf{v}) \cdot \mathbf{n}]\!] \,. \tag{6.106}$$

References

[1] J. E. Adkins, *Nonlinear diffusion: III. Diffusion through isotropic highly elastic solids*, Philosophical Transactions of the Royal Society, **256**(1964), pp 301-316.

[2] G. A. Ateshian, On the theory of reactive mixtures for modeling biological growth, Biomechan Model Mechanobiol, **6** (2007), pp. 423-445.

[3] R. J. Atkin and R.E. Craine, *Continuum Theories of Mixtures: Basic Theory and Historical Development*, Q. J. Mech. Applied Mathematics, **29**(1976), pp. 209-244.

[4] R. J. Atkin and R.E. Craine, *Continuum Theories of Mixtures: Applications*, J. Inst. Maths Applics., **17**(1976), pp. 153 - 207.

[5] R. M. Bowen, Theory of Mixtures, in Continuum Physics, Volume III, Academic Press, 1976.

[6] P. Chadwick, Continuum Mechanics: Concise Theory and Problems, Dover, 1999.

[7] S.A. Chester and L. Anand, A coupled theory of fluid permeation and large deformations for elastomeric materials, J. Mech. Phys. Solids, **58** (2010), pp 1879-1906. ALSO A thermo-mechanically coupled theory for fluid permeation in elastomeric materials: application to thermally responsive gels, J. Mech. Phys. Solids, **59** (2011), pp. 1978-2006.

[8] M. Biot, General theory of three-dimensional consolidation, J. Appl. Phys., **12** (1941), pp 155-164.

[9] R.P. Feynmann, R.B. Leighton and M. Sands, The Feynmann Lectures on Physics, 1963, Volume I, Chapter 43.

[10] A.Fick, Ann. der Phys., 94(1855), pp. 59

[11] P.J. Flory and J. Rehner, Statistical mechanics of cross-linked polymer networks. II Swelling, J. Chem. Phy., **11**(1943), pp. 521-526.

[12] P.J. Flory, Thermodynamics of high polymer solutions, J. Chem. Phy., **10**(1942), pp. 51-61.

[13] F.P. Duda, A.C. Souza and E. Fried, A theory for species migration in a finitely strained solid with application to polymer network swelling, J. Mech. Phys. Solids, **58** (2010), pp. 515-529.

[14] E. Fried and M.E. Gurtin, Coherent solid-state phase transitions with atomic diffusion: a thermomechanical treatment, Journal of Statistical Physics, **95**(1999), pp. 13611427.

[15] E. Fried and M.E. Gurtin, A unified treatment of evolving interfaces accounting for deformation and atomic transport with emphasis on grain-boundaries and epitaxy, Advances in Applied Mechanics, **40**(2004), pp. 1177.

[16] M.E. Gurtin, Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance, Physica D, **92**(1996), pp.178192.

[17] W. Hong, X. Zhao, J. Zhou and Z. Suo, *A theory of coupled diffusion and large deformation in polymeric gels*, J. Mech. Phys. Solids, , **56**(2008), pp. 1779-1793.

[18] M.L. Huggins, Solutions of long chain compounds, J. Chem. Phy., **9**(1941), pp. 440.

[19] R. Phillips, J. Kondev and J. Theriot, Physical Biology of the Cell, Chapter 15, Garland Science, 2009.

[20] K. Rajagopal and L. Tao, Mechanics of Mixtures, World Scientific, 1995.

[21] R. Skalak, G. Dasgupta, M. Moss, E. Otten, P Dullemeijer and H. Vilmann, Analytical description of growth, J. Theoretical Biology, Volume 94, (1982), pp. 555 - 577.

[22] R. Skalak, D.A. Farrow and A. Hoger, Kinematics of surface growth, J. Math. Biology, Volume 35, 1997, pp. 869-907.

[23] J . Stefan, Sber. Akad. Wiss. Wien., **63**(1871), pp. 63

[24] W. Hong, X. Zhao, J. Zhou and Z. Suo, A theory of coupled diffusion and large deformation in polymeric gels, J. Mech. Phys. Solids, , **56**(2008), pp. 1779-1793.

[25] L.R.G. Treloar, The Physics of Rubber Elasticity, Oxford University Press, 1975.

[26] C. Truesdell, *Sulle basi della thermomeccanica*, Rend. Lincei, **22**(1957), pp. 33

[27] C. Truesdell and R. Toupin, *The classical field theories*, in Handbuch der Physik, (S. Flugge, editor), Volume III/1, Springer Verlag, Berlin, 1960.

[28] C. Truesdell and W. Noll, *The nonlinear field theories of mechanics*, in Handbuch der Physik, (S. Flugge, editor), Volume III/3, Springer Verlag, Berlin, 1965.